The influence of storage environment on the fracture behaviour of acrylic bone cement

Hailey, Jacquolyn Lesley

Award date:
1993

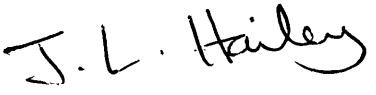
Awarding institution:
University of Bath

THE INFLUENCE OF STORAGE ENVIRONMENT ON THE FRACTURE BEHAVIOUR OF ACRYLIC BONE CEMENT

submitted by Jacquolyn Lesley Hailey, B.Sc.(Hons)

for the degree of PhD

1993



ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

ABSTRACT

Total joint replacement is a procedure which gives pain relief and renewed mobility to over 50,000 people each year in the U.K. alone. Whilst offering new hope to many of these people, approximately 10% of these prostheses fail within 10 years. It is thought that cement fracture could be one cause of the failure of the implant.

This study was primarily concerned with the effect of storage environment and time period on the work of fracture of Simplex P bone cement. It was found that the storage conditions had a significant influence on the work of fracture of bone cement. In particular, storage at body temperatures embrittled the cement, whilst storage in fluid media had a plasticising effect. These trends were related to post-curing chemical changes within the cement mass, specifically the absorption of low molecular mass species from the storage environments, and the leaching of residual monomer from the cement.

A significant decrease in the work of fracture of the bone cement was observed with long-term storage (2 years) in the fluid media. This decrease could not be attributed to post-curing chemical changes occurring within the cement mass. It is postulated that the decrease in the material's resistance to crack growth was a result of a process termed physical aging.

ACKNOWLEDGEMENTS

I am particulary grateful to my supervisors, Dr. Irene Turner and Mr. Tony Miles, for their support, advice and encouragement during the course of this project; thank you both. Thanks are also due to all the staff; academic, technical, secretarial, and administrative, in the School of Materials Science at the University of Bath. I am also grateful to Gareth Price of the School of Chemistry at the University of Bath for his help and advice with the chemistry aspects of this thesis. Thanks too are due to all the members, past and present, of "The Biomob" research group from the Schools of Materials Science and Mechanical Engineering. I really appreciated your thoughts and ideas guys, thanks for listening to me !

To all my family who have always been there for me, especially Mum, Dad, and Andrew. Thanks for your constant financial and emotional support, and for your patience and encouragement during the last twelve months. Also Gina, my dog, whose affection and loyalty will always be greatly appreciated

Thanks to all my friends and collegues in both Bath and Leeds for putting up with me whilst I went through stresses and strains of writing up.

To John Fisher for his encouragement, patience and understanding over the last twelve months. Sorry its taken so long boss !

I am also grateful to the SERC for funding this research and to Howmedica International for the additional support and the endless supplies of bone cement.

CONTENTS

GLOSSARY AND ABBREVIATIONS

Acetabulum - pelvic (or hip) socket

Arthroplasty - a replacement joint

Aseptic loosening - loosening in the absence of infection

DIC - differential interference contrast

Femur - thigh bone

Fully Cured Cement - bone cement which has been heat treated to remove any residual monomer

GC - gas chromatography

GPC - gel permeation chromatography

in vitro - in the laboratory

in vivo - in the body

Macrophage - a large scavenger cell which removes bacteria or other foreign bodies from blood and tissue

Necrosis - death

Normal Cement - bone cement prepared under typical clinical conditions

Phagocytosis - the engulfment and digestion of bacteria and other foreign particles by a cell

PMMA - polymethylmethacrylate

Prosthesis - an artificial replacement bodily part

SEM - scanning electron microscope

THR - total hip replacement

TJR - total joint replacement

TKR - total knee replacement

Trabecular bone - the porous bone inside the cortical walls

WOF - work of fracture

MATHEMATICAL SYMBOLS

Material's Property Symbols

K_{IC} - fracture toughness

M_n - number average molecular mass

M_w - weight average molecular mass

T_g - glass transition temperature

V_f - free volume

Statistical Symbols

n - number of samples

s - standard deviation

$t_{0.05}$ - Students t-distribution at the 95% level of confidence

$\bar{x}$ - mean value

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

In 1927 Rhom and Haas produced the first industrial acrylic, polymethylmethacrylate (PMMA) (Park, 1983). The use of acrylics as biomaterials began in the 1930s, when they were used as heat-curing denture bases. During World War II the scarcity of metals lead to the development of a self-curing acrylic cement for use as tooth fillings and caps (Lee, Ling and Pearson, 1981). It was not until 1958 that Sir John Charnley (advised by Dr Dennis Smith, a dentist) first used self-curing acrylic to secure the femoral component of a joint replacement. Today the primary use of such self-curing PMMA acrylics is as bone cements for fixation in orthopaedic surgery, where they are often used to secure prostheses into bone in the joint replacement procedure.

The first operation to successfully restore function to a hip joint, although not involving a prosthesis, has been credited to Anthony White in 1822 (Fifield, 1987). In 1891 Thomas Gluck began experiments on an artificial ball and socket joint made from ivory. By 1938 the ivory had been replaced with cobalt-chromium alloy (E. J. Haboush) or stainless steel (Philip Wiles), and the first total hip replacement was performed by Wiles (Coventry, Beckenbaugh, Nolan, and Ilstrup, 1974). However, it was not until Charnley began his work in the early 1960s that total hip arthroplasty was performed on any significant scale. Today some 750,000 total hip replacements are performed world-wide each year (Miles, 1989). In the UK alone the 1987 estimate for such operations was 42,500 (Bonfield, 1987), and today the figure is reputed to be over 50,000. This means that in Britain approximately half a million people have had a total joint replacement (Fisher, 1993).

Most hip replacements utilise a metal femoral component and a polymeric acetabular component: 70% of which are cemented into place using polymethylmethacrylate (PMMA) bone cement. A schematic diagram of a typical hip prosthesis is shown in Figure 1.1. The function of the cement is to hold the femoral and acetabular components firmly in place, to transmit the loads from the prosthesis to the underlying bone, and to act as a de-coupler between the mismatch in stiffness of the prosthesis

and bone (Ling, 1986). The cement achieves this not by acting as an adhesive, but by mechanical interlocking. PMMA has the ability to form a highly accurate replica of any mould into which it is cast. After polymerisation the mould becomes mechanically locked into the PMMA replica. Bone cement is thus able to model itself very closely to the porous structure of the bone into which it is cast, interlocking with the irregularities on the surface of the bone and the prosthesis (Lee, Ling and Pearson, 1981).

The main reason for joint replacement is because the natural joint has developed arthritis. In Britain one in seven people suffers from either osteo or rheumatoid arthritis, that is around 8 million people (Fifield, 1987). Although these diseases primarily affect the elderly, 2% of young adults suffer from a deformity of the hip joint (Katz, 1990). In 1987 an American health study reported that 10% of 15-24 year olds were already osteoarthritic, in other words had suffered some joint degeneration (Bonfield, 1987). The result of these diseases is excruciating pain and a loss in function of the joint, which when it affects the hip or knee joint means restricted mobility. For most of these people the joint replacement operation literally changes their lives, leaving them free from pain and completely mobile again. For example, Wiklund and Romanus (1991) assessed the quality of life of 56 patients before and 1 year after total hip arthroplasty, and found a significant improvement regarding pain, energy, sleep, and social isolation. In their study they found that the quality of life after joint replacement was in close agreement with that of a healthy reference group.

Despite the large numbers of joint replacement operations performed each year, there are still problems associated with the procedure. There is a 10% clinical failure rate in patients over the age of 65. This means that 90% of hip replacements, in this age group, have an average lifetime of 10 years before revision (replacement) is required. Unfortunately this lifetime decreases significantly with the lifetime of the implant, as joints are revised, and with heavier or more active patients. So there can be an

understandable reluctance by surgeons to perform joint replacement procedures on excessively overweight, or young active patients (below the age of around 45 years).

The current average lifetime for a hip prosthesis in a 65 year old patient is 12 years, but this has an error of plus or minus 12 years associated with it (Bonfield, 1993). For 45 year old patients, who are generally more active, the average life expectancy of the implant decreases to 5 years. Thus in some cases an artificial hip joint may last for 24 years, but unfortunately in others the prosthesis may fail immediately after the surgery, necessitating a revision operation. In addition to the extra trauma to the patient caused by a revision operation, there are also additional financial costs, the biggest being the operating time since at least two primary joint replacements can be performed in the time taken for one revision. The other major drawbacks to revision surgery are the unknown - the surgeon cannot necessarily know the appropriate course of action until the failed prosthesis has been removed and examined. Also there is an associated risk of fracturing the femur as the failed prosthesis can be extremely difficult to remove from the surrounding bone.

In 1988 approximately 12% of all the hip replacements performed in Britain were revisions (Public Eye, 1993), today this figure has risen to 33% (Bonfield, 1993). Clearly the reasons for failure of the prostheses need to be evaluated. The major long-term problem with cemented total joint replacement is aseptic loosening (this is loosening in the absence of infection). The mechanism of loosening is poorly understood, however, it is generally accepted that it is a two component problem, involving a biological and a mechanical phase (Pizzoferrato, Ciapetti, Stea and Toni, 1991). It is the mechanical phase of loosening which this project is concerned with. In particular, fracture of the bone cement mantle, a problem often associated with the mechanical component of loosening (Johanson, Bullough, Wilson, Salvati, and Ranawat, 1987).

Bone cement is a two component material, it is formed by mixing a pre-polymerised PMMA powder with a liquid methylmethacrylate monomer. This results in a structure which contains pre-polymerised PMMA beads in a recently polymerised PMMA matrix. Unfortunately bone cement is a significantly weaker material than commercially produced PMMA, which is polymerised at high temperatures and pressures. Bone cement, however, is hand mixed in the operating theatre under ambient conditions. The resulting material contains a relatively high percentage of residual monomer and porosity. This already weak material is then expected to interface with living bone. This leads to the entrapment of blood and bone debris, hence weakening the material further. It is therefore conceivable that failure of the cement could initiate the loosening process. Gross fracture of the bone cement mantle and micro-fracture of the cement at the interfaces between the implant and the bone are two possible failure mechanisms which will be discussed in more detail later.

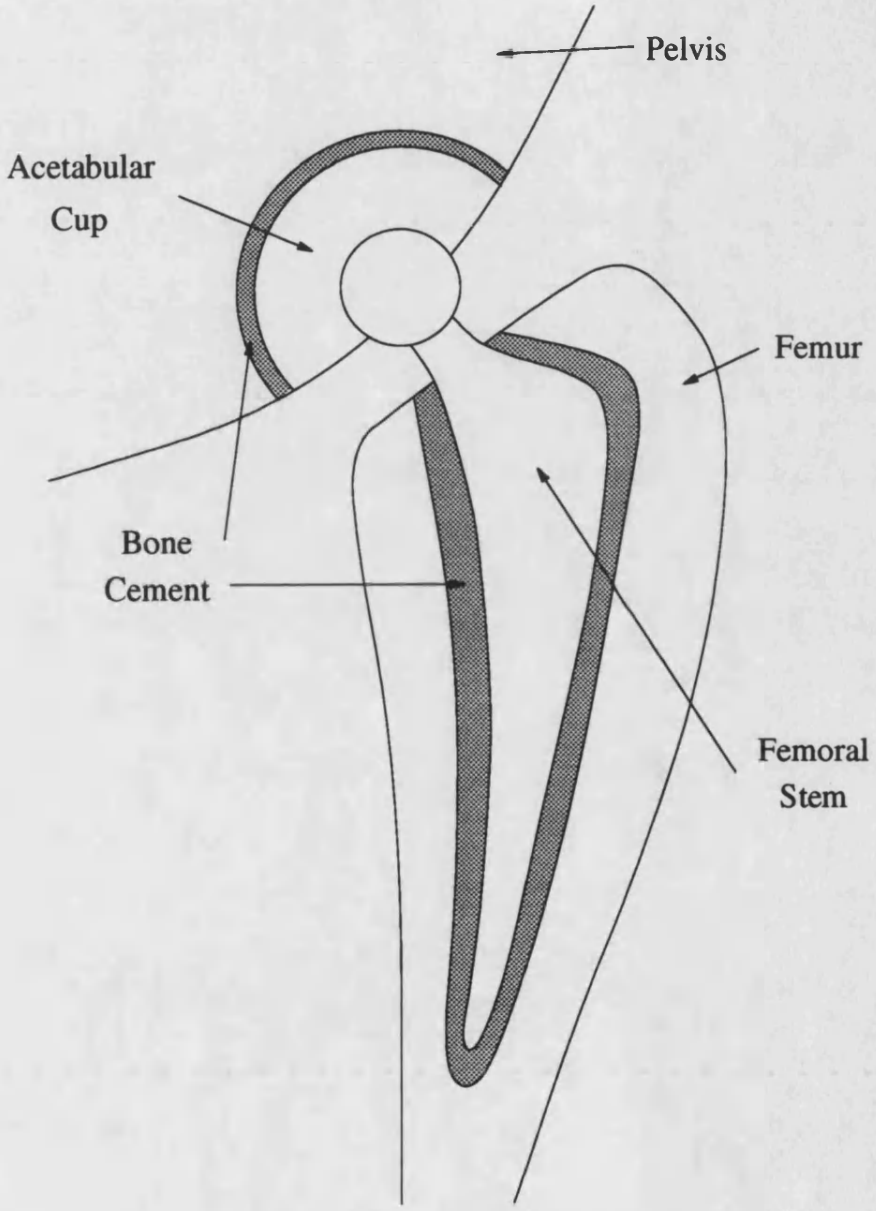
Three of the major standards used for materials testing, the American Society for Testing and Materials (ASTM), the British Standards, and the International Standards Office (ISO), all have specifications for the composition and testing of bone cements, which contain very similar tests for mechanical properties such as indentation and recovery, and compressive strength. However, given the acknowledged brittle nature of acrylic bone cements and their application, none of the above standards include other mechanical tests such as resistance to crack growth, bending tests, nor fatigue tests.

Extrapolation between the results of different studies is extremely difficult as even if the testing conditions of the studies are the same, variables such as speed and time of mixing, insertion conditions, pressurisation during setting and length of curing period can affect the mechanical properties of the cement, and these tend to be either not controlled or are not stated in the studies. Differences in specimen size, and rate and method of testing have also been found to influence the mechanical properties of bone

cement. Thus although many studies have looked at the effect of one or two variables upon the mechanical behaviour of bone cement, it is not possible to correlate the findings of these individual studies.

The aims of this project were thus to establish the effect of aging environment and time period on the fracture behaviour of Simplex P bone cement, and to relate these effects to the chemical and molecular changes occurring within the cement mass. The fracture behaviour of the cement was characterised by work of fracture (WOF) tests which were based on a test devised by Tattersall and Tappin in 1966 (Tattersall and Tappin, 1966). This involved loading a specimen notched to give a triangular cross-section in three-point bending. The apex of the triangle was loaded in tension and a crack propagated through the cross-section in a controlled manner. The energy required to initiate and propagate the crack gave the work of fracture of the specimen. Although this is not directly related to the fracture toughness of the material, it is a measure of the material's resistance to crack growth. The aging conditions were chosen to simulate the individual components of the physiologically environment so that the influence of each variable could be ascertained.

Figure 1.1: Schematic Diagram of a Total Hip Replacement



2. LITERATURE REVIEW

2.1 Total Joint Replacement

2.1.1 Reasons for Joint Replacement

The joints which are most commonly replaced are the major weight bearing ones; the hip and the knee. The most common reason for total joint replacement (TJR) is arthritis, around 8 million people in Britain suffer from the disease (Fifield, 1987). Both rheumatoid and osteoarthritis can lead to severe pain and lack of function of the joints. However, there are also other, less common reasons for joint replacement. Many post menopausal women suffer from a disease known as osteoporosis. This causes a thinning of the trabecular structure and hence weakening of the bone, which after severe trauma, for example a fall, can result in complex fractures of the femur (thigh bone) necessitating total joint replacement. Both arthritis and osteoporosis mainly affect the elderly, however, joint replacement can also be necessary for younger people, although it is much less common. In the young the main reasons for joint replacement are juvenile arthritis resulting in the pain and deformities as seen in elderly suffers. Also TJR may be necessary as a result of road traffic accidents or sports injuries which have caused either complex fractures or gross damage to the joint.

2.1.2 Joint Replacement Procedure

A schematic diagram of a total hip replacement (THR) is shown in Figure 1.1 and the operative procedure is detailed below. Firstly the head of the femur is removed and a cavity formed inside the bone shaft and also in the acetabulum. This is done by a processing called reaming where the bone is basically grated away. Both cavities are then washed with a sterile saline solution to clear away the blood and bone debris. If cement is to be used for the fixation, it would be mixed whilst the cavities were being cleaned, and thumbed (or injected) into the cavities once the doughy state was achieved. The femoral stem and the acetabular cup would then be inserted under moderate pressure to force the cement into the spaces in the trabecular bone so that it

forms a good interlock between the prosthesis and the underlying bone. If it is a cementless arthroplasty, then the prostheses would be forced into the cavities once the blood and bone debris had been removed. So the operative procedure causes a severe amount of trauma to the bone bed which is expected to then interface with the foreign prosthesis. Also the material at the interface with the bone (either the prosthetic components or the bone cement) is expected to interface with living biological tissue, and will thus be in contact with the resultant physiological fluids such as blood, fat and bone marrow.

Most TJRs are now based on a metallic component articulating against a polymer component. In artificial hip and knee joints the femoral component tends to be metallic, and the tibial or acetabular component is generally polymeric. The metals which are used are usually either stainless steel, cobalt chrome or titanium alloys, and the polymer generally tends to be ultra high molecular weight polyethylene (UHMWPE). Recently other material combinations have been developed to try to minimise wear of the articulating surfaces. These include ceramics such as zirconia and alumina in place of the currently used metals and modified polyethylenes.

2.1.3 Fixation

The femoral stem and acetabular cup are usually fixed in place either using PMMA bone cement, a porous coating (such as a titanium mesh or sintered titanium beads) or by achieving a very close fit (press fit) between the bone and the implant. All of theses methods of fixation rely solely on mechanical interlocking, there is no chemical bond formed. Screw threaded components are literally screwed into the bone, whereas press fit components fill the whole cavity and rely on a close fit between the bone and the implant to secure the prosthesis. Porous coatings such as sintered beads and wire meshes allow bone ingrowth and hence secure fixation. None of the above methods of fixation have any bonding, all the surfaces are chemically inert and the prostheses are only fixed mechanically. A new bioactive coating has recently been developed based

on calcium hydroxyapatite, the mineral component of bone. This is plasma sprayed onto the implants and when implanted allows some chemical bonding with the bone. The final method of fixation is PMMA bone cement, which in this country is the most popular method of fixation. Around 70% of joint replacements in Britain use cement and about 50% in the USA. As mentioned earlier bone cement still relies on mechanical interlocking to fix the prosthesis into the underlying bone, there is no chemical bonding between the cement and the bone. Cemented joint replacement offers the surgeon a less exacting operative technique, as the cement fills the gap between the stem and the bone cavity.

The cement, which is supplied as a polymer powder and a liquid monomer, are hand mixed by the scrub nurse in theatre. When the liquid is added to the powder it dissolves the surface of the polymer, releasing an initiator and thus starting the polymerisation of the liquid monomer. As the polymerisation process continues, the cement becomes highly viscous and doughy, it is then that it can be handled and is thumbed into the bone cavity where it sets and becomes hard.

2.2 TJR Failure

It has been reported (Lautenschlager, Stupp and Keller, 1984) that 10% of documented total hip replacements have problems with infection after surgery. In recent years, however, the incidence of infection has been dramatically reduced due to the use of antibiotic loaded bone cements and improved operating conditions. Most operating theatres now use down drafts of clean air and exhaust suits for the surgical staff to minimise bacterial contamination and infection. As mentioned in section 1 there is currently a 10% clinical failure rate of hip prostheses. (The failure rate in knees generally tends to be larger due to the higher demands made on TKR). The

major long term complication associated with total hip replacement today is aseptic loosening of the prosthesis (Moreland, 1988, Harris, McCarthy and O'Neill, 1982, and Pizzoferrato, Ciapetti, Stea and Toni, 1991).

2.2.1 Loosening

There has been much discussion in the literature about the definition of loosening, since some prostheses which appear loose on radiographs are mechanically stable, and others which appear stable on radiographs are mechanically loose (Brand, Pedersen and Yoder, 1986). Generally, however, loosening of TJRs is accompanied by pain and the development of a radiolucent line at the bone-implant interface (Rose and Litsky, 1989).

Various reasons have been suggested for loosening of hip and knee prostheses. These can be divided into two main categories ; mechanical failure of one the implant components, or biological failure as a result of a foreign body reaction to the prosthesis or its wear debris (Pizzoferrato, Ciapetti, Stea and Toni, 1991).

Today it is recognised that one of the major problems with joint prostheses is the foreign body reaction to polyethylene wear debris and small fragments of bone cement (Clarke and Campbell, 1988, Rose and Litsky, 1989, and Willert, Bertram and Buchhorn, 1990). Small particles of these two polymers are phagocytised by macrophages, activating the macrophages which then release chemical mediators. The release of these chemical mediators induces bone resorption, which in turn contributes to aseptic loosening (Clarke and Campbell, 1988, Chiba, Maloney, Horikoshi, McIntyre and Rubash, 1993, and Horowitz, Doty, Rapuano, and Burstein, 1993)

Malcolm (1988) observed microfractures of the trabeculae and suggested this as a possible cause of loosening. Fibrous encapsulation of the bone cement has also been suggested as a mechanism responsible for loosening. Foreign-body giant cells appear

to be attracted to the bone cement, this then causes bone resorption, followed by replacement with a fibrous layer (Freeman, Bradley and Revell, 1982). The reason for the attraction of the giant cells to the cement is not yet known, although several reasons have been suggested. Charnley (1975) suggested it that was due to particles of cement debris, which were generated as the cement moved relative to the bone. Freeman, Bradley and Revell (1982) support this view and also suggest leaching of the monomer from the cement mass as another possible cause. Thermal and mechanical damage of the bone have also been suggested as causes of bone resorption and hence fibrous layer formation (Ling, 1986, and Andersson, Freeman and Swanson, 1972).

The strength of the bone-cement interface depends on the nature and viability of the surrounding bone. This bone is constantly remodelling to adapt to the changing stress distribution, and often as a result, a fibrous capsule forms between the cement and the underlying bone, where there is micromotion present. It has been shown (Park, 1983) that the thickness of this capsule and hence the gap between the cement and the bone increases with time, in turn decreasing the strength of the bone-cement interface.

The long term stability of a cemented joint replacement depends upon the success and persistence of the mechanical interlock between the prosthesis and the underlying bone. Even in cases which were thought to have good initial fixation, loosening can develop years after the surgery. This late loosening has often been attributed to the bone cement for several reasons (Park, 1983);

i) bone necrosis at the bone-cement interface may occur due to the high exotherm during polymerisation

ii) leaching of residual monomer from within the cement may also cause bone necrosis due to its toxicity

iii) shrinkage of the cement mass during polymerisation or a poor distribution of cement within the bone cavity may result in inadequate fixation of the prosthesis

iv) the cement is weakened in tension due to the presence of internal pores.

2.2.2 Clinical Evidence of Bone Cement Failure

There are two situations in which loosening of the implant can occur due to cement fracture. The first is when there is gross, or macroscopic fracture of cement mantle, the second is when microfracture of the cement at the interfaces between the implant or the bone occurs. The result of gross fracture of the cement mantle is that a reduced amount of the cement mantle is available to support and transmit the loads generated during locomotion. This will lead to higher contact stresses in the region of the implant system which is still supporting the loads and loosening of the implant will occur. Microfracture of the cement at the interfaces may create small particles which can cause failure of the arthroplasty as a result of the foreign body reaction to the small particles, or due to excessive wear in the articulation zone. Microfracture of the cement can also lead to micromotion at the interfaces. When this occurs at the bone-cement interface bone necrosis can occur which will also lead to loosening of the prosthesis. Hence both macroscopic and microscopic fracture of the cement mantle can result in aseptic loosening of the arthroplasty.

2.2.2.1 Microfracture of the Cement Mantle

It has been suggested that since the monomer is highly soluble in fat, the bone cement surface which is in contact with the bone will not be completely polymerised (Jasty and Smith, 1992). This could lead to poor binding of the pre-polymerised beads, which would permit easier microfracture of the cement at this surface.

Johanson, Bullough, Wilson, Salvati and Ranawat (1987) found evidence of cement particles in the fibrous membranes surrounding explanted prostheses. The authors postulated that in porous trabecular bone, where the cement intrusions were large, that fracture of the bone could occur. However, in dense cortical bone it was postulated that cement failure would occur, see Figure 2.1. The authors suggested two

mechanisms by which cement fracture could occur, either (1) fracture of large cement intrusions into pores within the bone, or (2) abrasion of the surface of the cement. It was thought that the debris generated by the first mechanism could be an important feature of the mechanical phase of the loosening process. Whereas the second process was thought to be the cause of the fibrous layer, the biological phase of the loosening process.

Jasty and Smith (1992) also suggested that micromotion at the cement interfaces might occur due to the differences in the elastic moduli of the three materials (prosthesis, cement and bone).

2.2.2.2 Macroscopic Fracture of the Cement Mantle

Other authors have considered radial cracks in the cement mantle which have been associated with prosthesis loosening (Stauffer, 1982, Miller, Burke, Stachiewicz and Kelchay, 1977, and Jasty, Maloney, Bragdon, O'Connor, Haire and Harris, 1991). Subsidence of the femoral component has also been associated with cracking of the cement (Paterson, Fulford and Denham, 1986, and Weber and Charnley, 1975). This can lead to thigh pain and in extreme cases, instability of the prosthesis. Cement failure can also initiate fracture of the femoral component due to inadequate support of the prosthesis (Sih, Matic and Berman, 1981, and Martens, Aernoudt, DeMeester, Ducheyne, Mulier, DeLangh and Kestelijn, 1974).

2.2.2.3 Fatigue Fracture of the Cement Mantle

In the body failure of the cement will probably be by a fatigue mechanism due to the cyclic loading, rather than fast fracture from impact loading. However, it is impossible to simulate the *in vivo* fatigue situation in the laboratory. Not only would this involve a very complex loading arrangement, but it would also require an excessively large number of cycles to failure. The complexity of the situation is illustrated when the literature on fatigue of bone cement is considered (Krause and Mathis, 1988, and

Johnson, Provan, Krygier, Chan and Miller, 1989). A wide range of testing conditions have been employed, so comparison cannot be made between studies. If further variables such storage environment are introduced, then the situation becomes very complex indeed. Hence in this study it is necessary to first characterise a much simpler property, the basic fracture properties of one type of bone cement. We have chosen Simplex P radiopaque which is in widespread clinical use.

2.3 The Composition and Structure of Acrylic Bone Cement

Acrylic bone cement is generally supplied as a sterilised two component kit, containing a 40g sachet of a dry powder and a 20ml ampoule of a liquid component. The powder consists of pre-polymerised spheres which are mixed with the liquid monomer, resulting in a two phase cured material containing pre-polymerised beads embedded in a recently polymerised matrix. The bone cement used in this study was Simplex P radiopaque bone cement supplied by Howmedica International, and details of its composition are given both in Table 2.1, and below.

The powder component of Simplex P consists of pre-polymerised spheres which are a mixture of styrene-methylmethacrylate copolymer and polymethylmethacrylate homopolymer. These spheres are produced by suspension polymerisation of the monomers using benzoyl peroxide as the initiator (Brydson, 1975). Sufficient benzoyl peroxide is used to produce the spheres, so that there is an excess of benzoyl peroxide remaining in the powder, available to initiate the polymerisation of the liquid monomer (Pearson and Jones, 1978). The liquid component of the cement consists of methylmethacrylate monomer, which, when added to the powder, swells the spheres to release the benzoyl peroxide. The methylmethacrylate monomer contains N,N-dimethyl-p-toluidine, which activates the polymerisation reaction by decomposing the

benzoyl peroxide rapidly to produce the free radicals necessary for the polymerisation of the monomer. Polymerisation of the monomer during storage is prevented by the addition of hydroquinone to absorb any free radicals which are created in the liquid. The large quantities of free radicals which are generated by the initiator and activator during polymerisation of the monomer overcome the stabilising action of the hydroquinone (Park, 1983). When the monomer and the powder are mixed, the monomer swells the pre-polymerised beads releasing the benzoyl peroxide enabling it to react with the N,N-dimethyl-p-toluidine to produce free radicals which allow the monomer itself to begin polymerising. The polymerisation process is terminated by combination, chain transfer or disproportionation. During the polymerisation process, as the polymer chains become longer the cement dough becomes more viscous and the diffusion of the last few monomer units to the ends of chains is retarded. Thus some unreacted methylmethacrylate monomer units become trapped within the cement mass due to the slow diffusion rate of the chain radicals, leading to a 3% residual monomer content (Haas, Brauer and Dickson, 1975, and Brauer, Termini and Dickson, 1977). There is no evidence of crosslinking in either the powder component or the cured cement (Kusy, 1978, and Black, 1988), and the polymer chains in the binding matrix are essentially linear (Black, 1988). The powder component of the radiopaque cement also contained the radiopaque agent, barium sulphate.

2.3.1 Copolymerisation with Styrene

It has been shown (Haas, Brauer and Dickson, 1975) that styrene constitutes only 2.3% of the powder component of radiolucent Simplex P (approximately 2.1% of the radiopaque powder). The authors reported that the copolymer contains 2.8% styrene and that 83.3% of the radiolucent powder (75% of the radiopaque powder) is copolymer.

The reason for the incorporation of the styrene-methylmethacrylate copolymer into Simplex P bone cement is to improve the mixing properties of the material (Haas,

Brauer and Dickson, 1975, and Brauer, Termini and Dickson, 1977). It has also been reported (Haas, Brauer and Dickson, 1975) that copolymerisation of the acrylic with styrene may decrease the degradation of the cement caused by sterilisation irradiation, and may reduce the polymerisation exotherm. These authors suggested that although styrene has been used in acrylics to reduce water absorption, the amount present in Simplex P bone cement is unlikely to have such an effect.

It has been suggested (Kusy, 1978) that copolymerisation of Simplex P bone cement with styrene may weaken the material, since polystyrene has an inherent flaw size of 1.3mm which is approximately 25 larger than that of PMMA. However the author also acknowledged that polystyrene has a fracture energy which is an order of magnitude greater than that of PMMA. Johnson and Jones (1991), however, found that the incorporation of 5% styrene into methylmethacrylate-ethylmethacrylate and methylmethacrylate-butylmethacrylate copolymers had no effect on K_{IC}. The authors also found that the addition of styrene did not alter the glass transition temperature (T_g) of the material.

2.4 Leaching of Residual Monomer from Bone Cement

In a study to assess which tissues the monomer had the greatest affinity for, Willert, Frech and Bechtel (1975) added recently polymerised (between dough time and setting time) bone cement to human bone marrow and showed that the quantities of monomer which evaporated into the tissue were highest in the fat, lowest in the red blood cells, and intermediate in the bone marrow fibres and cells. Albrektsson (1985) performed experiments to ascertain the effect of the leaching of residual monomer from bone cement into bone tissue, and found that a more severe tissue reaction

occurred if the tissue was rich in fat cells. The author attributed this observation to the fat solubility of the monomer.

Petty (1980) evaluated the amount of methylmethacrylate monomer present in the bone tissue surrounding a 5mm cube of PMMA bone cement after the cement had polymerised *in vivo*. The author found that immediately after implantation the average methylmethacrylate concentration in the bone next to (within 1mm) the bone cement was 0.14% by volume. This concentration was similar 1 hour after implantation, but began to fall with longer periods after implantation and with distance away from the bone cement, by 6 hours after implantation no methylmethacrylate was detected in the tissue immediately adjacent to the bone cement. The author suggested that although other studies monitoring the amount of monomer released into the blood supply indicated that there was insufficient monomer to cause systemic toxicity (see below), their study showed that the concentration of monomer in the bone tissue next to the cement mass was sufficient to have an adverse effect on human cells and proteins.

Several authors have shown that low levels of methylmethacrylate monomer can also be detected in the blood of patients undergoing joint replacement operations (Bloch, Haken and Hastings, 1971, Gentil, Paugam, Wolfe, Lienhart and Augereau, 1993 and Healy, Wasilewski, Pfeifer, Kurtz, Hallack, Valerio and Valeri, 1993). Bloch *et al* (1971) reported monomer levels of 10 - 20ppm in 10% of the patients studied, and a level of 100ppm in one patient. The authors also wrote that "the presence of monomer did not appear to follow a consistent pattern", and attributed this to the lack of continuous sampling. Gentil *et al* (1993) monitored the methylmethacrylate plasma concentrations from 30 seconds up to seven minutes after implantation of the cement during hip replacement, and found that the peak concentration occurred after approximately 2 minutes. The maximum monomer concentration was 12.3μg/ml with an average value of approximately 3μg/ml. The authors also found that seven minutes after implantation of the cement, the average monomer concentration had fallen to

0.2μg/ml. Healy *et al* (1993), although unable to detect any methylmethacrylate in the systemic blood of patients undergoing total joint arthroplasties, did find a significant amount of monomer in the blood drained from the joints during surgery. Fifteen minutes after the drain was inserted the authors reported values of 69μg/ml and 414μg/ml of methylmethacrylate in the blood of hip and knee replacements respectively. The authors also found that the levels of monomer were highest 5 minutes after insertion of the drain, and after 6 hours were undetectable. A study by Bayne, Lautenschlager, Greener and Meyer (1977) to evaluate monomer release as bone cement cured *in vitro* supported these clinical observations that the maximum level of monomer in the blood stream occurs not at insertion but 1-5 minutes after insertion, probably as a result of the setting exotherm. The variation between the above results of the different workers has been attributed to differences in the techniques of cement preparation, sites of blood sampling, the time of sampling and the methods of obtaining the measurements (Gentil *et al*, 1993), and to the degree of vascular damage during surgery (Linder, Harthon and Kullberg, 1976). However, all the studies clearly show that methylmethacrylate monomer does leach into the blood surrounding the implant during total joint replacement.

Brauer, Termini and Dickson (1977) found that if a sample of radiolucent bone cement was stored in water at 37°C for 4.5 months without stirring, the residual monomer content decreased from its initial value of 2.7% to 1.4%.

Basker, Collier, Smith, Bartle, Frere and Wong (1989) studied the influence of water immersion on the residual monomer contents of several dental resins, by measuring the amount of monomer in both the resin and the surrounding water. The authors found that although specimens which were stored in water lost more monomer than those stored in air, there was no change in the monomer content of the storage water with time. It was therefore concluded that the reduced monomer content of the resins was not a result of the leaching of the monomer into the water. The authors suggested

that the more rapid decrease in monomer content of the dental resins when immersed in water was due to continued curing of the cement because of the exclusion of oxygen, which is known to inhibit the polymerisation of methylmethacrylate (Venz and Dickens, 1991 and Looney and Park, 1986). This inhibition of the polymerisation was attributed to the diffusion of oxygen into the cement and the subsequent combination of the oxygen with the free radicals (Looney and Park, 1986).

Several of the studies in the literature have talked about two types of residual monomer, one which is water soluble and one which is not (Smith and Bains, 1956, and Brauer, Termini and Dickson, 1977). Smith and Bains (1956) suggested that the water extractable monomer may have been associated with the surface of the cement due to a greater degree of polymerisation in the central region as a result of the higher polymerisation exotherm during curing in this region. The authors also suggested that the non-water extractable monomer may have consisted of molecules trapped some how by the long polymer chains.

Schoenfeld, Conard and Lautenschlager (1979) immersed specimens of bone cement into an aqueous solution 10 minutes after mixing the powder and the monomer. The amount of monomer released into the solution was then evaluated periodically by gas chromatography of the storage solution. It was found that the monomer was released rapidly during the first 15 minutes after insertion, then stabilised to a steady value of 0.049g, which corresponded to 2.1% by weight of the initial monomer content of the specimen, and 0.7% by weight of the cured material. Schoenfeld *et al* (1979) attributed the rapid release of monomer during the first 15 minutes of immersion to the curing reaction of the cement. The authors referred to another paper (Scheerer, Swartz, Norman and Phillips, 1964) in which specimens had been stored in air and had also not seen any significant monomer release after the end of the curing cycle, due to some residual monomer remaining in the cement after curing. It was postulated that this monomer was trapped within the bulk of the cement. Schoenfeld *et al* (1979)

wrote that the "release of the residual monomer would require bulk diffusion to the surface such that this monomer would be released over long periods of time in amounts that would be negligible compared to the initial release of monomer prior to completion of the curing reaction." The authors concluded that the period of concern regarding patient safety and the release of the toxic monomer was between the insertion and the setting of the cement, which is probably as a result of the polymerisation exotherm during setting.

Brauer, Termini and Dickson (1977) also measured the amount of monomer which had leached into the surrounding water medium for samples of cement which were placed in aqueous contact three minutes after mixing. These authors also found that the most rapid release of monomer occurred within the first 30 minutes after mixing, and attributed this to the curing cycle of the cement. It was again suggested that the residual monomer is leached into the aqueous media much more rapidly during the period before it sets. The amount of monomer leached into the solution was also similar to that obtained by Schoenfeld *et al* (1979), 0.67% for the latter and 0.4% by Brauer *et al* (1977).

The study by Linder, Harthon and Kullberg (1976) was very similar to those by Brauer, Termini and Dickson (1977) and Schoenfeld, Conard and Lautenschlager (1979). Specimens of Simplex P radiolucent bone cement were immersed into an aqueous medium 4 minutes after the start of mixing, and the amount of monomer leaching into the solution was monitored periodically. Linder *et al* (1976) also reported similar findings to those of the other two groups, that there was a rapid rise in monomer concentration of the aqueous solution for the first 3 minutes after immersion with a subsequent gradual decrease in concentration which the authors attributed to monomer evaporation from the storage solution.

There will be an element of residual monomer in the cured bone cement which has not come from the liquid monomer, as the powder component itself contains some unreacted methylmethacrylate. Brauer, Termini and Dickson (1977) reported a value of 0.28% residual monomer in the powder component of radiolucent Simplex P. Since in radiopaque Simplex P bone cement 10% of the powder is barium sulphate, it is thought that in the samples used in this thesis the powder component would have contained approximately 0.25% residual monomer. Brauer *et al* (1977) attributed the presence of residual monomer in the powder to the fact that "during its commercial manufacture, some monomer does not reach initiating sites during the polymerisation and is entrapped in the powder particles." The value of 0.28% methylmethacrylate content in the powder component means that in the cured cement there will be approximately 0.2% monomer which has come from the powder component and not the added monomer liquid, since the powder makes up approximately two thirds of the cured cement (Jefferiss, Lee and Ling, 1975).

2.5 The Molecular Mass of Bone Cement

Haas, Brauer and Dickson (1975), and Brauer, Termini and Dickson (1977) evaluated the molecular mass of both the powder component of the cement and also samples of the cured material which had been stored in air. They found that the molecular mass distributions for the powder and the cured material were very similar, but that there were slight differences in the number and weight average molecular masses of the two materials. The number average molecular masses of the powder and the cured cement were reported to be 44,000 and 51,000 respectively, and the weight average molecular masses of the powder and the cured cement were found to be 198,000 and 242,000 respectively. Bayne, Lautenschlager, Compere and Wildes (1975) found the average number of monomer repeating units to be 453 in the cured cement and 321 in the

powder component. Since the molecular mass of methylmethacrylate monomer is 100 these correspond to number average molecular masses of 45,300 for the cured cement and 32,100 for the powder component. Hence it appeared from all these studies that the cured cement had a slightly higher molecular mass than the isolated powder component. This effect has also been shown in another study by Huggett, Bates and Packham (1987). Bayne, Lautenschlager, Compere and Wildes (1975) also showed that the degree of polymerisation of the matrix material was approximately twice that of the pre-polymerised powder. The authors attributed this to the fact the polymerising monomer formed chains which were much longer than those in the pre-polymerised beads and suggested that the conditions for the polymerisation of the matrix may have been conducive to autoacceleration. It was therefore concluded that the matrix which is formed on mixing the powder and monomer has a higher molecular mass than that of the pre-polymerised beads of the powder component. Brauer, Termini and Dickson (1977) offered the explanation that when the monomer was added to the powder some grafting or branching occurred at active polymer sites as well as the formation of new polymer chains, a theory also supported by Smith (1961). But it has also been reported (Black, 1988, and Bargar, Brown, Paul, Voegli, Hseih and Sharkey, 1986) that the polymer chains which make up the matrix material are essentially linear.

Bargar, Brown, Paul, Voegli, Hseih and Sharkey (1986) found that generally there was no significant difference between the molecular mass of bone cement samples which had polymerised *in vitro* and similar samples which had been polymerised and stored *in vivo*. The only significant difference in the molecular masses of any of the samples was with *in vivo* cement from the proximal region of the implant, which was significantly less (8-10%) than either the *in vitro* samples or those from the distal and plug regions. The authors related this trend to an observed inferior strength of the *in vivo* cement samples from the proximal region compared with those from the distal and plug regions and the *in vitro* samples.

Chain scission, and hence a reduction in the molecular mass of a polymer, can occur either by free radical depolymerisation or by hydrolysis (Black, 1988). Most medical grade polymers are chosen for their stability as well as their physical properties, however, with long implantation times low degradation rates become important. For example, reductions in the molecular mass of UHMWPE have been observed after long periods of implantation (Black, 1988).

2.6 General Mechanical Properties of Bone Cement

Charnley (1970) listed the properties of self curing PMMA which make it suitable for use as a bone cement. These included its insolubility in the physiological fluids, the relatively short setting time (6-10 minutes) and the fact that this is not affected by entrapment of blood, the tendency to expand on setting rather than contract, an adequate strength of the set material, that the components can be easily sterilised, and that a composite material can be formed without the need to modify the surfaces of the pre-polymerised beads. Among the properties which Charnley cited as requiring improvement are; reduction of the polymerisation exotherm, reduction of the toxicity of the monomer, increased expansion on setting, and resistance to surface degradation.

The dissolution process is influenced by the distribution of particles, the particles themselves (composition and shape), the molecular mass of the polymer, and the powder to liquid ratio (Smith, 1971). Within a few minutes the consistency of the mixture has change from a lumpy sand-like slurry to a smooth mouldable dough. As the polymerisation process continues the dough becomes stiffer, which is when the mobility of the monomer becomes impaired (Beverly, 1990). As already discussed in section 2.3, the result is a fairly large residual monomer content in the "cured" cement. This residual monomer has a plasticising effect on the cement (Wang and Pilliar,

1989a), (which will be discussed later in this section), thus making it an important consideration when dealing with the fracture behaviour of this material.

The resulting structure of the cured cement is a two-phase one. The cement mass consists of pre-polymerised beads stuck together with recently polymerised monomer (Smith, 1961, Kusy, 1978, Kusy, Mahan and Turner, 1976, and Cameron, Mills, Jackson and Macnab, 1974). The effect of these spheres embedded in the monomer matrix is to strengthen and toughen the cement. Hence the two-phase structure of bone cement has relevance when dealing with the fracture properties of the material.

Although industrial polymethylmethacrylates, such as Plexiglas and Perspex, are chemically very similar to acrylic bone cements, the mechanical properties of the two materials are vastly different, as can be seen in Table 2.2. This is because commercial PMMA is formed using higher temperatures and pressures than are possible to achieve during TJR, to yield a non-porous, transparent material with a much higher degree of polymerisation than the self-curing bone cements. The bone cements are manually mixed under ambient conditions by the theatre nurse at the time of surgery. The microstructure of the two materials is also very different. Industrial PMMA is a homogeneous material, whereas bone cement is a composite structure consisting of the pre-polymerised beads in the recently polymerised matrix. The large variability in the values for the various mechanical properties given in Table 2.2 is an indication of the difficult in obtaining specimens with reproducible properties.

The mechanical properties of various brands of bone cement have been compared in several studies. Kusy (1978) showed that the elastic modulus, ultimate tensile strength and elongation to failure were similar for CMW, Palacos R, Sulfix-6 and Simplex P bone cements, but that they were inferior to those of industrial PMMA. This same study also found that the fracture energies of the four cements were similar to that of industrial PMMA, but that the inherent flaw size was 5 times larger in the bone

cements than in PMMA (see Table 2.2). It has also been reported by Lautenschlager, Stupp and Keller (1984) that dental acrylics have lower mechanical properties than heat cured PMMA due to their defect content. Dental resins were reported to have a lower fracture surface energy due to a larger inherent flaw size, and a lower molecular mass.

The mechanical properties of polymers can be altered by the absorption of low molecular mass chemicals such as water or lipids, or the desorption (leaching out) of low molecular mass species which remain after polymerisation or are the result of chain scission. The changes in the mechanical properties are basically the result of changes in the plasticity or ductility of the polymer as a result of the absorption or desorption processes (Black, 1988). Some examples of these processes and their effects are given in Table 2.3. Plasticisers which are found in implantable polymers are generally low molecular mass residual chemicals, such as residual monomer, and absorbed water and low molecular mass lipids. Black (1988) reported that the effect of such plasticisers was generally to increase toughness and elongation to failure, but decrease the melting point, hardness and tensile strength of the polymer concerned.

The ingress of the fluids would act as a plasticiser by molecules of liquid keeping the polymer chains apart so that they could slide over each other more easily. This would ease the deformation of the cement, and thus reduce the elastic modulus of the material. A consequence of a reduction in the elastic modulus of the cement would be an increase in the fracture resistance of the material as it would require more energy to fracture the cement due to some energy being absorbed in the deformation process.

All polymers are visco-elastic to varying degrees, resulting in a dependence of their mechanical properties on the rate and temperature of testing. The visco-elastic nature of polymers is due to strong covalent bonds which form the backbone of the polymer chains and the weaker intermolecular bonds which exist between the chains. Small

strains will only break the weaker intermolecular bonds, allowing motion of the polymer chains. Higher strains will first cause an uncoiling of the main polymer chains followed by breaking of the covalent bonds and subsequent fracture of the polymer. If the rate of testing is increased then the modulus of the polymer will increase and it will behave in a more brittle manner, if the test temperature is increased then the modulus will decrease and the polymer will behave in a more ductile manner.

A review of the mechanical properties of bone cement undertaken by Saha and Pal (1984), indicated that the visco-elastic nature of bone cement and its fracture properties both required further investigation. It was reported that storage of cement samples in air had little effect on the properties of the material, but that storage in fluids had a plasticising effect on cement.

2.6.1 Influence of Porosity on the Mechanical Properties of Bone Cement

The presence of porosity within the cement mass has been shown by several authors to have a detrimental effect on the mechanical properties of bone cement. Bayne, Lautenschlager, Compere and Wildes (1975) showed that the removal of porosity from bone cement influences the diametral tensile strength to a greater degree than it does the compressive strength. This was attributed to the fact that pores being pulled open during tensile tests, act as stress concentrators and degrade the mechanical properties of the material to a greater extent than do compression tests where the pores are being closed up. DeWijn, Slooff and Driessens (1975) showed that there was approximately a 30% reduction in the flexural strength and 40% reduction in the impact strength of bone cement samples due to porosity.

Bayne, Lautenschlager, Compere and Wildes (1975) showed that a clear, non-porous acrylic bone cement could be produced if radiolucent cement dough was polymerised under very high pressures (27.6MPa). The resultant material was found to have a

higher density and higher compressive and diametral tensile strengths, but the molecular mass of the material cured under high pressure was the same as that of a similar sample which was cured at ambient pressure. The authors therefore attributed the increased strength with high pressure curing to the absence of porosity.

Defects or pores within a material have been reported to have many weakening effects on the material containing them (Lautenschlager, Stupp and Keller, 1984). They can act as stress concentrators causing the material to fail below its recognised strength value. The presence of pores also decreases the effective cross sectional area of the material which is capable of withstanding the applied loads. Pores can also act as crack initiation sites, and aid crack propagation. Kusy (1978), however, suggested that the presence of porosity within the cement structure "should not be over-emphasized" since "globular pores may create minimal stress concentrations" and hence have a very small effect on the mechanical properties of the material.

Cameron, Mills, Jackson and Macnab (1974), DeWijn, Slooff and Driessens (1975), and Haas, Brauer and Dickson (1975) suggested that the porosity in the cement was due to a combination of air entrapment during mixing and to the evaporation of pockets of trapped monomer and contaminating body fluids during curing. It has also been suggested that the decomposition of benzoyl peroxide during setting releases carbon dioxide which may contribute to the microporosity of the cement mass (Lautenschlager, Stupp and Keller, 1984). Another theory for the formation of pores within the cement mass is that as the monomer dissolves the pre-polymerised beads, the doughy cement mass expands. However, as the cement begins to set, the polymerising monomer contracts but the cement mass is too rigid to contract with it, so internal stresses form which also lead to the formation of internal porosity (Lautenschalger, Stupp and Keller, 1984). Another source of defects within the material could come from the residual monomer. If this leaches out from the cement

mass during storage, then additional porosity may develop within the cement (Kusy, 1978).

Various techniques have been used to try to reduce the porosity content of bone cements. These include centrifugation during the early stages of the curing cycle, pressurisation of the curing cement dough, vacuum degassing of the powder component prior to mixing and vacuum mixing of the cement dough (Black, 1988). These methods have been found to greatly reduce the porosity content of the cements and consequently lead to modest increases in the strength of the material.

2.7 Review of the Fracture Properties of Bone Cement

The fracture toughness of various brands of bone cement have been evaluated using compact tension (Sih and Berman, 1980, Wright, Sullivan and Arnoczky, 1984, and Rimnac, Wright and McGill, 1986), Charpy (Freitag and Cannon, 1976, Stark, 1979, and Gutteridge, 1993), and short-rod specimens (Wang and Pilliar, 1989a). Double torsion specimens have also been used, achieving slow crack growth and hence allowing crack growth rate versus stress intensity factor plots to be obtained (Owen and Beaumont, 1979, Owen and Beaumont, 1980, Beaumont, 1979, Beaumont and Young, 1975, and Beaumont and Young, 1977). It was found from these studies using slow crack growth tests, that bone cements undergo slow crack growth at stresses significantly lower than their ultimate tensile strengths.

The effects of various additions such as radiopaque agents and antibiotics, on the mechanical properties of bone cements have also been investigated. The majority of investigators found that barium sulphate additions weakened the cement when it was tested under ambient conditions (air at 21°C), decreasing the resistance to crack

growth (Freitag and Cannon, 1976, Owen and Beaumont, 1979, Owen and Beaumont, 1980, Beaumont, 1977, Beaumont, 1979 and DeWijn, Slooff and Driessens, 1975). Freitag and Cannon (1976), however, also found that the barium sulphate reacted with their bovine serum testing environment and thus increased the fracture toughness of the cement. Cooke, Tsai, Marrero and Yashuda (1991) showed that the addition of zirconium dioxide to bone cement reduced the ultimate tensile strength by 25%. However, when the surface of the zirconium dioxide was chemically treated to promote bonding of the radiopaque agent to the polymer, the authors found that the reduction in the tensile strength was only 4%. Owen and Beaumont (1980), Beaumont (1977), and Beaumont (1979) attributed these reductions in the fracture toughness and tensile strength to the opening up of cavities around each weakly bonded radiopaque particle. It was suggested that the crack propagates by the linking up of these voids, a process termed void coalescence. Beaumont (1977) suggested that the coalescence occurred by the elongation of the cavities and a tearing of the recently polymerised PMMA matrix between them. Owen and Beaumont (1979) and Owen and Beaumont (1980) showed that additions of antibiotic particles (which are a tenth of the size of the barium sulphate particles) to bone cement have no effect on the fracture behaviour of the material.

Differences in the fracture behaviour of various brands of cement have been reported by several workers. Wright, Sullivan and Arnoczky (1984) found that Palacos exhibited a larger fracture toughness than Zimmer cement. Rimnac, Wright and McGill (1986) confirmed this, finding that Palacos had a higher fracture toughness than both Simplex and Zimmer cements. Both Stark (1979) and Freitag and Cannon (1976) reported that Zimmer cement exhibited higher fracture toughness when compared with Simplex P cement. However, Wang and Pilliar (1989a) found that, after storage for 60 days in water at 37°C, Simplex P cement showed superior fracture toughness when compared with that of Zimmer LVC.

Rimnac, Wright and McGill (1986), and Wang and Pilliar (1989a) have investigated the effect of centrifugation on the fracture properties of bone cement. Both groups of workers found that centrifugation did not alter the fracture toughness of the cement. Wang and Pilliar (1989a) also concluded that K_{IC} was not controlled by porosity content alone. Beaumont and Young (1975), however, found that K_{IC} was dependant on fabrication pressure, which in turn controlled the void content. The authors postulated that the pores would act as stress raisers and possible crack nucleation sites. Gharpuray, Keer and Lewis (1990) reported evidence of cracks emanating from pores and also from the spherical pre-polymerised beads, which appeared to be acting as inclusions. The authors suggested that in cement these beads are weakly bonded to the matrix, and that this weak interface would strengthen the cement by forcing the crack to deviate around the spheres.

Contradictory results about the effect of the environment on the fracture properties of bone cement have also been reported. Beaumont (1979) concluded that the environment played no part in the fracture process. Beaumont and Young (1975), Beaumont and Young (1977), and Owen and Beaumont (1980) however, all reported that the crack velocity decreased when tests were performed in saline solution as opposed to air. It was concluded that this was due to the formation of a plastic zone ahead of the crack tip (Owen and Beaumont, 1980, and Beaumont and Young, 1975). Crazes at the crack tip have also been observed by Beaumont and Young (1975). Freitag and Cannon (1976) found that the fracture toughness of the cement was increased when tests were performed in bovine serum. Environmental effects were also examined by Wang and Pilliar (1989a), who concluded that the effect of storing specimens in water depended on the processing and nature of the cement.

It was obvious when reviewing the literature that there had been no standardisation of the fracture test procedures. The above mentioned authors had used several different test methods. There was a lack of data on the fracture properties after long-term

storage, and the individual influences of isolated components of the physiological environment had not been evaluated. The various workers had not tried to ascertain if there were any differences between storage at elevated temperatures as opposed to storage at room temperature, or between storage in the various fluids used (water, Ringer's solution and bovine serum). Considering the relatively high fat content in the bone cavities which the cement is expected to interface with, it was surprising that there had been no work to evaluate the effect of storage of cement in lipid solutions. Clearly these are all areas which require further investigation and will be covered within this project.

2.8 Influence of Storage Environment on the Mechanical Properties of Cement

Smith (1961) showed that both water absorption and high residual monomer contents decreased the tensile strength of dental acrylic denture base materials. After storage for 14 days in water at 37°C specimens of dental acrylic had absorbed approximately 0.7% by weight of water, and this had the effect of reducing the tensile strength by 9%. Smith (1961) also found that there was an 8% decrease in the ultimate tensile strength of a self curing dental resin with a residual monomer content of 2% compared to a similar resin containing 0.2% residual monomer, this decrease was doubled when 4% of the monomer was retained within the structure.

Bargar, Brown, Paul, Hseih and Sharkey (1986) reported no differences in the flexural strength, strain or modulus between cement specimens which had been stored in air and those which had been stored in saline for up to 8 weeks. The authors also showed that the failure strain of these *in vitro* samples was 30-40% less than that for cement which had been polymerised and stored *in vivo*. The modulus of the *in vitro* samples

was, however, found to be 20-50% higher than that of the *in vivo* samples. There were no observed differences in the flexural strength of the various cement samples. The authors found slight but significant changes in the strength and the modulus of both the *in vitro* and the *in vivo* cement samples with time. For both of the properties there was an increase (3-5% for strength and 5-10% for modulus) from 0 to 2 weeks, then a decrease (2-3% for strength and a return to the zero time value for modulus) between 2 and 8 weeks storage.

Looney and Park (1986) compared the effect of *in vitro* storage of cement in saline at 37°C with that of storage *in vivo* in canine femoral canals. The authors found that although the *in vivo* samples required a longer time than the laboratory samples to reach full cure, both sets of samples had attained almost maximum strength within 2 weeks. There was a dramatic increase in the strength and modulus of rupture over the first 2 weeks of storage, after which there was no further increase in the strength, but there was a gradual decrease in modulus of rupture over the following 6 months.

Lee, Ling and Vangala (1977) found that the compressive strength of bone cement which was cured in physiological saline at 37°C changed with curing time. The authors showed an increase in strength between mixing and storage for 7 days, followed by a large decrease at 6 months and a smaller further decrease at 12 months.

Venz and Dickens (1991) reported that prolonged storage of dental resins in water results in a reduction of both the strength and the elastic modulus of the material. It has also been shown that the presence of blood within bone cement decreases the elastic modulus and flexural strength of the material (Holm, 1977).

Kusy (1978) showed that the elastic modulus was decreased by a quarter by storing samples of bone cement in water at 37°C for 10 months, and that the tensile strength was decreased to half its original value. In general the author found that the fracture

energy increased slightly after storage in the water, but that the inherent flaw size increased by approximately four times. This was supported by Causton (1975), and Hill, Bates, Lewis and Rees (1984) who all showed that the ingress of water into cement increased the inherent flaw size and the fracture energy of the cement. This increase in the inherent flaw size has been attributed to ability of water to promote crazing in PMMA (Wang and Pilliar, 1989, and Hill *et al*, 1984). It was suggested by Wang and Pilliar (1989) that the ingress of water may have the effect of either increasing K_{IC} or decreasing K_{IC}. An increase in K_{IC} could occur due to the increase in fracture energy as a result of the greater ductility of the cement. Whereas a reduction in K_{IC} would result from the stress concentrating effect of the absorbed water clusters which promote the crazing.

Haas, Brauer and Dickson (1975) carried out a study to assess the influence of setting and ageing temperature on the mechanical properties of bone cement. The authors performed indentation and recovery tests on bone cement samples which had set and been aged at 25°C, set and aged at 37°C, and set at 7°C but aged at 37°C. It was found that the samples which had been set at 7°C had the highest indentation and lowest recovery values of the three sets of specimens for the first few hours. However, after aging for a minimum of twelve hours the indentation had decreased and the recovery increased to similar values as for the group of samples which were set and aged at 37°C. The samples which were set and aged at 21°C had initial indentation and recovery values which were between those of the two other groups of specimens, however, after a few hours aging the indentation was much higher and the recovery much lower than either of the other two groups of samples. It was concluded that lower polymerisation and storage temperatures lengthen the time required for the mechanical properties of the cement to reach a steady state, due to a lower degree of polymerisation being obtained. If however, the cement is polymerised at a lower temperature, full mechanical properties can be obtained by subsequent storage at a higher temperature for a period of time.

2.9 Improvements to Conventional Cements

It is evident from the literature discussed so far, that acrylic bone cement does have certain limitations, particularly with respect to its biocompatibility and its long term mechanical stability. Bone cement comes under the same category as drugs in terms of its clinical and laboratory testing prior to public release. Hence the development of a completely new material to replace acrylic bone cement would prove to be very costly, particularly since cement is highly successful in providing short term fixation (up to 10 years). For these reasons various groups of workers have investigated modifications to both the chemistry, and the mechanical properties of the existing cements, in an attempt to reduce the incidence of aseptic loosening.

Pearson and Jones (1978) have successfully reduced the polymerisation exotherm of bone cement by substituting some of the pre-polymerised beads for glass microspheres which in turn reduced the amount of monomer required, with no observed loss in compressive strength. The authors also experimented with the addition of hydroxy ethyl methacrylate to the liquid component to increase the swelling of the cement when it was immersed in water. It was thought that this may have improved the mechanical interlocking of the cement within the bone cavity. The use of mixed acrylates in the liquid component instead of 100% methylmethacrylate was found to decrease the modulus, and thus increase the elongation at break in compression, without causing any significant losses in compressive strength. Finally, the authors found that the addition of carbon fibres to the cement increased both the modulus and tensile strength of the material.

Brauer, Steinberger and Stansbury (1986) experimented with alternative inhibitors and accelerators to improve the biocompatibility of their modified bone cement, reduce the setting time, and increase its strength. Attempts to reduce the polymerisation exotherm were also made by the authors, by the incorporation of higher molecular mass

methacrylates and the addition of a chain transfer agent. Although there was no deterioration in the physical properties with the addition of the latter chemical, it was found that the incorporation of higher molecular mass methacrylates reduced the strength of the resultant bone cement.

Almost all the improvements which have been made to bone cements in the past have had associated drawbacks. For example, the use of low viscosity cements improves cement penetration into the trabeculae of the bone and hence was thought to improve the bone-cement interfacial shear strength. However, the enhanced cement penetration also means that a greater quantity of bone comes into contact with the cement thus potentially increasing the amount of bone necrosis due to the polymerisation exotherm and the leaching out of residual monomer. This may well lead to a thicker fibrous membrane between the cement and the bone, thus decreasing the interfacial shear strength. Other authors (Pearson and Jones, 1978, Wright and Robinson, 1982, and Topoleksi, Ducheyne and Cuckler, 1992) have attempted to improve the mechanical properties of bone cements by fibre reinforcement, which have on the whole been successful in increasing the strength, fracture and fatigue resistance of the cement. Unfortunately the reinforcing agents tend to impair cement penetration into the underlying bone, thus decreasing the strength of the mechanical interlock between the cement and the bone.

2.10 Review of the Tattersall-Tappin Test

The chevron-notched bar, rod and bend-bar specimens, see Figure 2.2, were developed to determine the fracture toughness of brittle materials. These specimens are in widespread use for fracture toughness testing of ceramics, rock, high-strength metals, composites and other brittle materials. The original paper by Tattersall and Tappin in

1966 has itself been cited around 300 times. Chevron-notched specimens have been successfully used by several authors (Barker, 1977, Turner, 1973, and Rogers and Moyle, 1988) to find the fracture toughness or the work of fracture of commercially produced PMMA. The test procedure has also had accepted use with biological material. In 1970 Piekarski first used the Tattersall-Tappin test to investigate the fracture of bone tissue. Since then it has been used by Moyle (1978), and Moyle and Bowden (1984) to evaluate the work of fracture of canine and human bone respectively. Mayer, Moyle and Sauer (1983) have used the technique to find the work of fracture of porous high-density polyethylene implants, and the fracture toughness of dental resins has also been evaluated using short rod, chevron-notched fracture toughness specimens (Neihart, Li and Flinton, 1988). The fracture toughness of bone cement samples has been studied using short rod specimens (Wang and Pilliar, 1989a, Wang and Pilliar, 1989b, Perek and Pilliar, 1992, and Lewis, 1992), and the work of fracture of bone cement has been evaluated by Watson, Miles and Clift (1990) using the Tattersall-Tappin test. An advantage of the short rod specimen, when dealing with bone cement, is that specimens of dimensions approaching the cross-section of bone cements used *in vivo* can be produced. Typically the thickness of the cement mantle around a prosthesis is 2-5mm (Meyer, Lautenschlager and Moore, 1973), whereas conventional fracture specimens are considerably larger than this. It has been shown that the mechanical properties of bone cement are dependent on the specimen size as a result of different polymerisation exotherms due to the variations in the amount of cement needed for the specimens (Bargar, Brown, Paul, Voegli, Hseih and Sharkey, 1986, and Brown, Sharkey, Bargar, Paul, Voegli and Hseih, 1984).

The chevron-notched specimens have several advantages over conventional fracture toughness specimens (Newman, 1984);

1) the specimens are small and inexpensive,

2) they require no fatigue pre-cracking,

3) the notch guides the crack path,

4) the test procedure is simple, thus making it an ideal quality control test.

However, the specimens also have their drawbacks;

1) the thickness of the specimens may cause limitations,

2) there may be notch machining difficulties.

With the specimens used for this project the first drawback did not present a problem, as bars of bone cement could be easily cast. Also specimens were required which were of a similar thickness to that of the cement mantle *in vivo*, and this could be easily achieved with the Tattersall-Tappin test specimens. Bone cement is much easier to machine than other brittle materials such as ceramics and composites, and a relatively consistent notch geometry could be achieved with the use of a purpose built notching jig. Thus the second drawback to the Tattersall-Tappin test was also easily overcome.

One of the unique features of a chevron-notched specimen used in the Tattersall-Tappin test is the extremely high stress concentration at the crack tip. It is because of this, that the loads required for crack initiation are much smaller than those required for complete catastrophic failure of the specimen, and that propagation of the crack can be controlled by the use of a constant cross-head speed. Minimal energy is lost in plastic deformation elsewhere in the sample, virtually no energy is absorbed by the testing machine, and no energy is lost as kinetic energy due to specimens "flying off" as with impact tests. Thus the integration of the load-displacement curve gives the work which has gone entirely into the creation of the fracture surfaces, the work of fracture (WOF) (Moyle, Welborn and Cooke, 1978).

A typical load-displacement curve for the Tattersall-Tappin test can be seen in Figure 2.3. From this diagram it can be seen that as the load increases, the specimen and testing machine store elastic strain energy which is equal to the area under the load-

displacement curve (AB). When a crack is initiated the load falls, and the specimen and machine begin to lose their stored strain energy (BC). The region BC corresponds to rapid crack extension as the stored energy is lost. This is because initially the rate of strain energy release is greater than the energy required to generate the new fracture surfaces (Davidge and Phillips, 1972). After a crack has been initiated, it continues to grow in a controlled manner (CD). There is insufficient stored elastic energy in the specimen-machine system to totally fracture the specimen, so the crack propagation is then controlled by the strain rate (or cross-head speed) of the machine.

Although the work of fracture is not equivalent to the fracture toughness of a material, it is a measure of the resistance of the material to crack growth. It has been suggested (Harris, 1989) that the work of fracture is a more appropriate measure of the resistance to crack growth of composite materials, due to the energy absorbing failure mechanisms of composites.

Table 2.1 : Composition of Simplex P Radiopaque Bone Cement

Component	Quantity
POWDER	
Polymethylmethacrylate homopolymer	14.81 w/o
Methylmethacrylate-styrene copolymer	74.07 w/o
Benzoyl peroxide	1.25 w/o
Barium sulphate	9.88 w/o
LIQUID	
Methylmethacrylate monomer	97.51 v/o
N,N-Dimethyl-p-toluidine	2.48 v/o
Hydroquinone	75±15 ppm

w/o = weight percent

v/o = volume percent

Adapted from Hansen and Jensen (1990) and Park (1983)

Table 2.2 : Comparison of the Mechanical Properties of Bone Cement and Industrial PMMA

Mechanical Property	Bone Cement (Simplex P Radiopaque)	Industrial PMMA (Plexiglas G)
Elastic Modulus (GPa)	1.3 - 3.1	2.5 - 3.3
Tensile Strength (MPa)	28 - 46	48 - 76
Compressive Strength (MPa)	62 - 95	76 - 131
Fracture Strain (%)	1.4 ± 0.3	8.4 ± 0.9
Fracture Energy (J/m^2)	260 ± 60	130 ± 390
Mean Inherent Flaw Size (mm)	0.37	0.048
Density (g/ml)	1.2	1.18

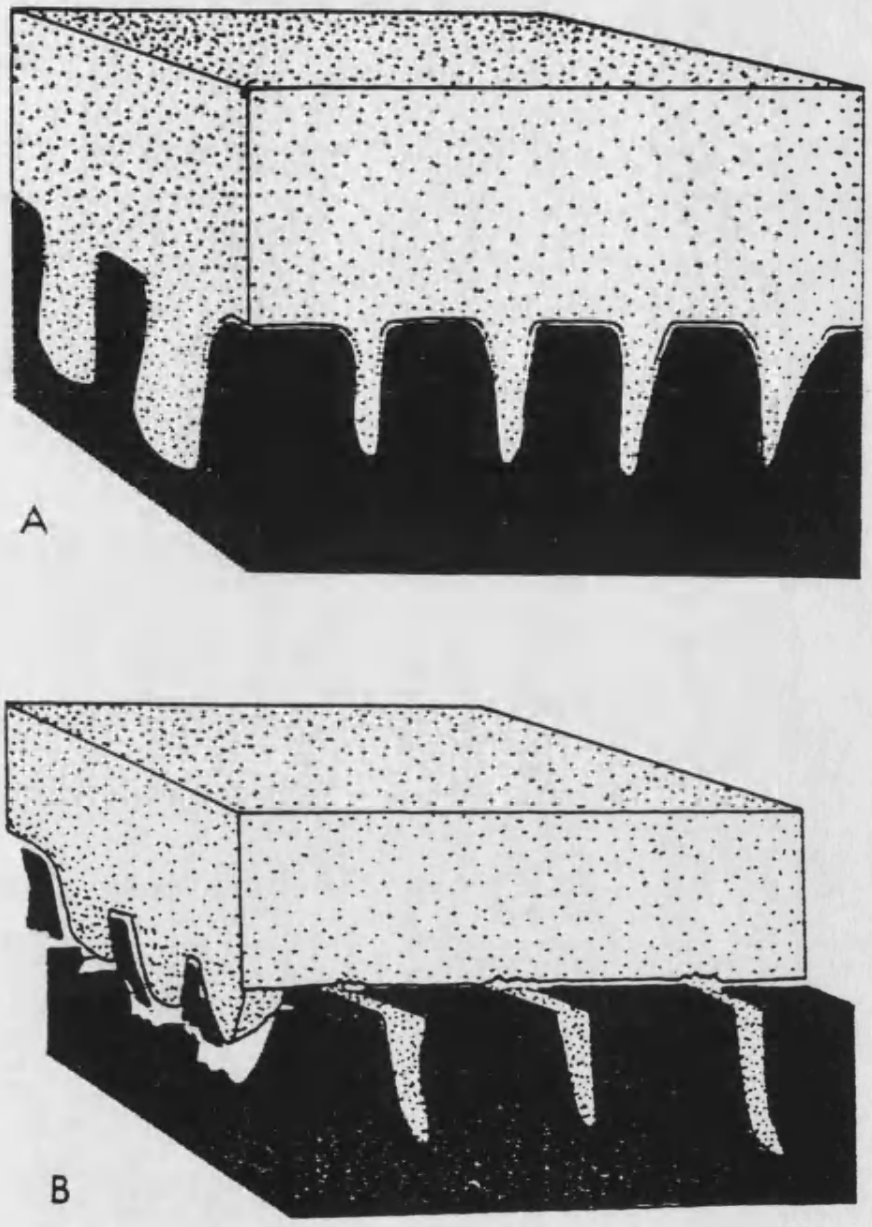
Adapted from Kusy (1978), Lautenschlager, Stupp and Keller (1984), and Haas, Brauer and Dickson (1975)

Table 2.3 General Effects of Degradation on the Mechanical Properties of Polymers

Degradation Mechanism	Effect on Modulus	Effect on Strength
Chain scission	Decrease	Decrease
Cross-linking	Increase	Increase
Absorption	Decrease	Increase*
Leaching	Increase	Decrease

* Extreme amounts of absorption can induce crazing and loss of integrity.

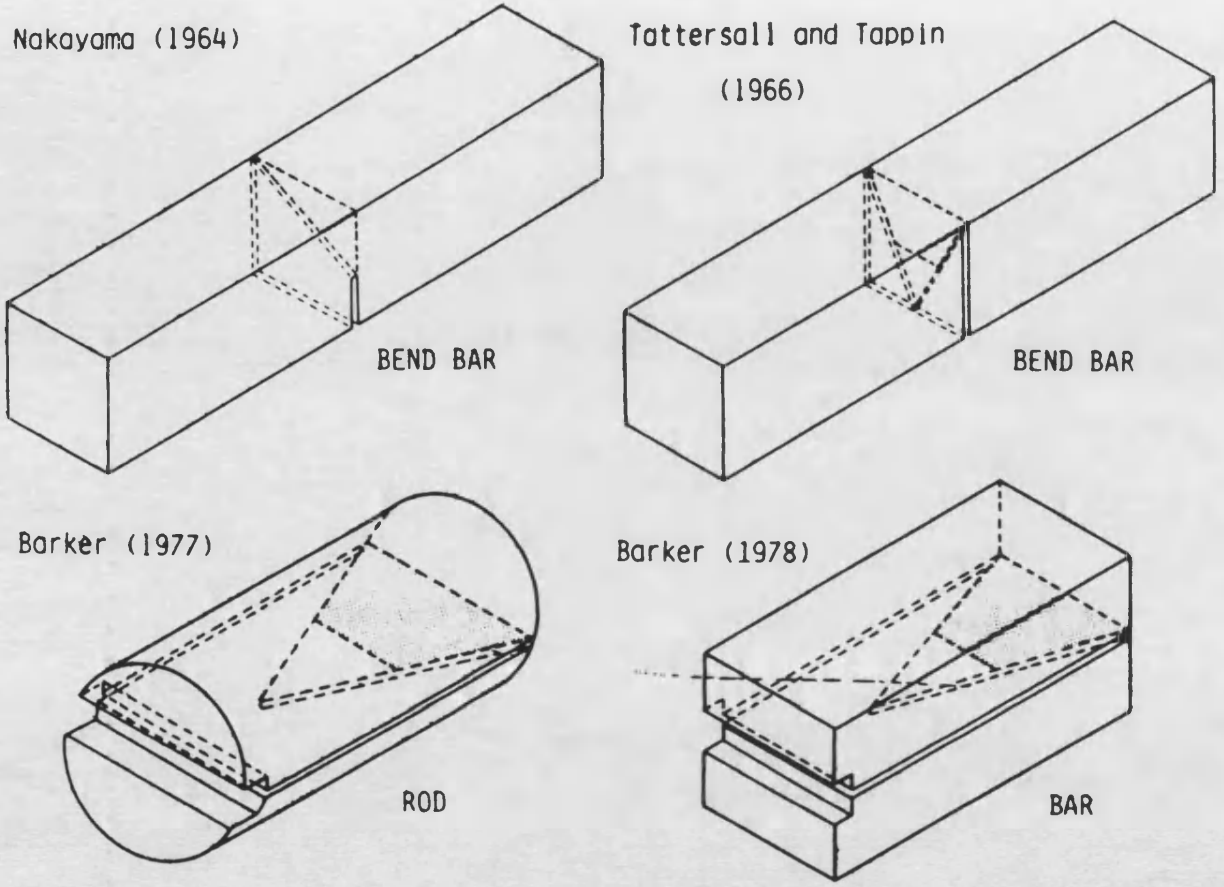
Adapted from Black (1988)



(A) Three-dimensional model of a bone-cement interface, with cement (stippled) above and bone (solid) below. To the left, large cement intrusions penetrate porous bone and, to the right, small cement intrusions are restricted by dense bone. (B) Mechanical failure: If the model in Figure 11A is loaded, such that significant motion occurs, the porous bone on the left will fail, and the slender cement intrusions on the right will fail.

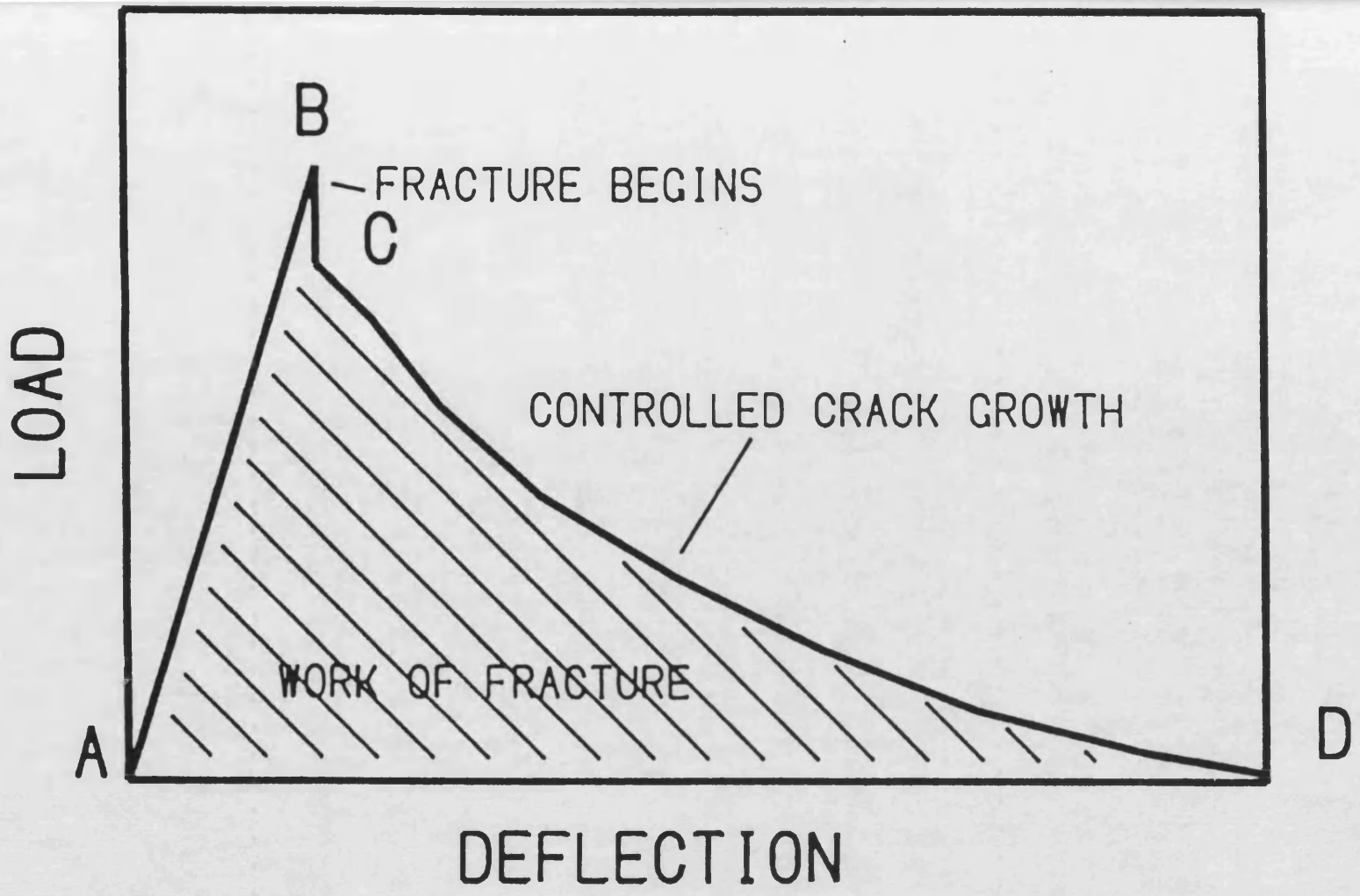
Figure 2.1 : Proposed Mechanism for Fracture of the Cement Mantle at the Bone-Cement Interface.

(After Johanson, Bullough, Wilson, Salvati, and Ranawat, 1987)



Various chevron-notched fracture specimen configurations.

Figure 2.2 : Geometry of Various Chevron Notched Specimens. (After Newman, 1984)



Schematic load–deflection curve.

Figure 2.3 : Load-Displacement Curve for a Tattersall-Tappin Test. (After Watson, Miles, and Clift, 1990)

3. EXPERIMENTAL METHODS

3.1 Introduction to the Experimental Programme and Test Methods

The various experiments carried out during this study generally tended to form a logical sequence. The data from one experiment led to the development of further investigatory strategies designed to improve the understanding of trends observed in the data. It therefore seems useful to comment in this chapter on some of these observed trends and how they led to further experimentation, in order that the development of the experimental programme can be appreciated. In this section the experimental programme will be discussed and the logic behind the various studies will be presented. The specific details of the experimental techniques used in the study will follow in the rest of this chapter.

The stated aim of the project was to evaluate the effect of the *in vivo* environment on the fracture behaviour of polymethylmethacrylate (PMMA) bone cement. The fracture resistance of the cement was characterised by the work of fracture (WOF) test devised by Tattersall and Tappin (1966). (see sections 3.2 and 3.3.4). This fracture test was developed specifically for brittle materials and is based on achieving controlled crack growth throughout the bulk of the specimen. It was thought that *in vivo* the cement would be more likely to fail due to a slow crack growth process, for example fatigue, than from impact loading. Hence this type of fracture test was thought to be more representative of the clinical failure mode than the conventional rapid fracture tests.

Due to the complex nature of the physiological environment it was decided to isolate the various components, to ascertain the influence of each variable of the *in vivo* environment on the fracture resistance of the cement. Details of the storage environments which were used in the study are discussed in section 3.3.3.

Whilst studying the WOF of the acrylic cement, it became evident that the residual monomer in the cement was interacting with the environments in which it was being stored. For this reason another project was set up where the monomer was eliminated as a variable, and the cement was fully cured before the influence of the storage environment on the WOF was studied. The technique for the preparation of the fully cured samples is given in section 3.3.2.

Since the fracture resistance of the cement had been studied solely with the WOF test which relies on achieving controlled crack growth, a series of rapid fracture tests were set up (see section 3.3.5). The aim of these tests was to check whether the trends which were observed with the WOF test were also apparent when the cement was subjected to catastrophic failure.

The results from the WOF tests indicated that the storage media were diffusing into the cement. This environmental ingress into the cement samples was monitored using the simple weight change experiment described in section 3.4.

It was the interactions of the monomer and the storage media which led to the development of the gas chromatography technique discussed in section 3.5. The aim of this element of the project was to analyse the residual monomer content of the cement under different storage conditions.

Long term storage of the fully cured cement was found to lead to a degradation in the resistance to crack growth. One theory for this involved hydrolysis of the cement leading to main chain scission of the polymer chains. This theory was investigated by analysing the molecular mass of samples of cement using the gel permeation chromatography technique discussed in section 3.6.

The fracture surfaces of various cement samples were examined using the microscopy techniques described in section 3.7.

3.2 The Tattersall - Tappin Test Technique

The fracture technique used in this study was based on the test devised by Tattersall and Tappin (1966). This test procedure involved loading chevron-shaped notched specimens in three-point bending. The chevron notch reduced the cross-section in the centre of the test piece from a square to an isosceles triangle, see Figure 3.1. The apex of the triangular cross-section was placed in tension, thus causing a crack to initiate due to the extremely high stress concentration. This stress concentration meant that the crack was initiated at a load much less that required for complete catastrophic failure. The increasing cross sectional area through the thickness of sample prevented rapid catastrophic fracture and caused the crack to propagate in a controlled manner, at a rate governed by the cross-head speed of the testing machine.

An idealised load-displacement curve for this test is shown in Figure 3.2. The curve shows that the fracture process involved three distinct phases. Region AB corresponds to the region of elastic deformation and stored elastic strain energy, region BC corresponds to the crack initiation, and region CD corresponds to the controlled crack growth. It was argued by Tattersall and Tappin that the total work done in fracturing the specimens was the summation of the crack initiation and crack propagation energies, i.e. the area under the load-displacement curve. The area under the curve gave the total energy of fracture for that particular specimen, this energy then had to be standardised by dividing through by the fracture surface area. The value thus obtained was the work of fracture (WOF), in Joules per metre squared (J/m^2), for that particular material.

3.3 Development of the Experimental Technique for Fracture Tests

3.3.1 Normal Sample Preparation

One complete pack of Simplex P radiopaque bone cement was mixed manually, according to the manufacturer's instructions, at approximately 1 Hz in a non-reactive bowl until the end of doughing time (approximately 4 - 5 minutes). The cement dough was then thumbed (as a surgeon would thumb it into the bone cavity) into the PTFE mould shown in Figure 3.3. Four bars of cement were produced from each batch of cement with dimensions 5mm x 5mm cross-section and 220mm in length. After curing for 30 minutes, in a press under minimal pressure, the cement bars were removed from the mould and placed into one of the selected storage environments.

3.3.2 Preparation of Fully Cured Samples

The fully cured specimens were mixed and cast using the same protocol as the normal specimens, see above. However, after curing for 30 minutes under ambient conditions, the specimens were removed from the mould and placed in an oven at an elevated temperature. It had been suggested (Beverley, 1990) that holding the cement above the glass transition temperature (T_g), 110°C, for approximately 12 hours would increase the mobility of the monomer sufficiently for continued curing to occur. Beverley (1990) believed that this heat treatment would reduce the residual monomer content of the cement from approximately 3% to approximately 0.5%. The cement specimens were therefore placed in an oven at 115°C ± 2°C for 15 hours ± 10 minutes. On removal from the oven the samples were allowed to cool in air under ambient conditions for approximately 1 hour, after which they were immersed in one of the various storage environments.

3.3.3 Storage Conditions

Eight different storage environments were used, these consisted of four different storage media and two temperatures. The media were as follows ; distilled water to simulate a simple liquid environment, Ringer's solution to introduce the physiological salts, Intralipid (an intravenous drip feed solution marketed by KabiVitrum Ltd.) which provided a reproducible fat solution to simulate the fat in the bone cavity, and air as a control. These media were stored in sterile glass jars and maintained at two different temperatures ; ambient, 21°C ± 1°C, and body, 37°C ± 1°C. The storage times studied ranged from 1 day up to 2 years for the normal cement, and from 1 week to 16 months for the fully cured cement. The glass storage jars were regularly shaken (at least weekly) to agitate the solutions and disperse their contents. The lipid solution also had to be changed approximately every six months as the solution went off, none of the other solutions were changed during the course of the study.

3.3.4 Work of Fracture Test Method

After storage for the required time period, the 220mm long bars of cement were cut into test pieces 50mm long. Immediately prior to testing the test pieces were removed from the storage environment and notched. A chevron type notch was introduced into the bar of cement using a purpose made notching jig and a slitting saw with a preset notch depth shown in Figure 3.4. The apex of the notch was sharpened using a razor blade, as described by Beaumont and Young (1975). This procedure ensured a sharp crack tip and hence very high stress concentrations at the tip. Approximately 10 - 12 specimens per environment were then tested in slow three point bending under ambient conditions (in air at 21°C ± 1°C).

The notched specimens were loaded on an Instron 1122 test rig, see Figure 3.5, using a constant cross-head speed of 0.5mm/min. This test speed was comparable with that recommended by Tattersall and Tappin (1966). The load versus displacement was recorded both on the chart recorder of the Instron and digitally

on a computer. A software package had been specially written to record the data and integrate the load - displacement graph, hence giving the area under the curve. This area was then converted into the total work done in fracturing the specimen, or the fracture energy. As expected the computer calculated fracture energy was much more accurate than the area measured from the Instron chart paper. The fracture energy could be measured to an accuracy of 0.1Nmm using the computer and associated software.

The work of fracture was calculated by dividing the fracture energy obtained from the computer by the combined area of the two fracture surfaces. The area of the triangular fracture surfaces was obtained by multiplying the base and height of the triangle together and dividing by two. (It was assumed that the fracture surface was a perfect triangle). A Joyce Loebl Magiscan 2A image analyser was used to measure the base and height of each triangular fracture surface. The camera of the magiscan was attached to a Wild M3Z optical microscope and the specimens illuminated with oblique lighting as shown in Figure 3.6. This arrangement allowed a television image of the fracture surface to be produced in which the surface was magnified by 3x. A microscaler was then used to frame the fracture surface giving the base and height dimensions of the triangle, see Figure 3.7. This was found to give a more accurate determination of the fracture area than measurements made by visual inspection. Measurements of the height and width of the triangular fracture surfaces could be made to an accuracy of 0.1 mm.

3.3.5 Rapid Fracture Test Method

The specimens for this test were mixed, cast, and stored using the same protocol as for the normally prepared work of fracture samples. After storage for the required time period, the specimens were notched to a depth of 1mm using a cutting tool with a radius of 0.25mm, see Figure 3.8. The specimens were then subjected to rapid three point bending (impact testing), under ambient conditions, using the pendulum type Hounsfield Plastic Impact Machine shown in Figure 3.9. This

machine recorded the energy absorbed in fracturing the specimens. Measurements of the fracture energy could be made to an accuracy of 2Nmm. This fracture energy was then normalised to a work of fracture value by dividing the fracture energy by the area of the fracture surfaces which were generated. These fracture areas were measured on the Joyce Loebl Magiscan 2A using the same experimental set-up as for the work of fracture (WOF) specimens.

3.4 Method for Measuring Environmental Ingress

The rate of environmental ingress was evaluated for both normal and fully cured bone cement. The samples were mixed and cast using the same protocol as that for the work of fracture test specimens (see sections 3.3.1 and 3.3.2). The specimens were weighed immediately prior to storage and this initial mass was recorded. Six samples of each of the two types of cement were immersed into each of the eight storage environments used for the fracture tests (see section 3.3.3). The mass of all the specimens was then monitored periodically.

The specimens were weighed using the methods described in ISO 4049 (1988) and in ASTM F451-76 (1976). This involved removing the specimen from the storage media, blotting dry with absorbent paper and waving in the air for fifteen seconds, before recording the mass of the specimen. The mass was then converted into a percentage weight change from the original mass during the storage period.

3.5 Gas Chromatography Technique

A summary of the gas chromatography experimental technique is presented in Appendix A.

3.5.1 Details of the Equipment

Analysis of the residual monomer content of the bone cement samples was initially performed using similar conditions to those described by Brauer, Termini and Dickson (1977). However, problems were encountered when trying to separate the peaks of the methylmethacrylate monomer and the ethylmethacrylate internal standard on the resultant chromatograms. Therefore modifications to the above mentioned operating conditions were adopted.

The residual monomer content of the bone cement was determined using a Pye Series 104 gas chromatograph with flame ionisation detection (FID). The detector temperature was 250°C and the oven temperature was 150°C. Nitrogen carrier gas was used at a flow rate of 45cm^3/min through a column containing a stationary phase of 5% FFAP coated onto Chromosorb. Chlorobenzene was used as the solvent for the polymer, and the internal standard was hexane. A Hewlett Packard HP3390A Integrator was used to calculate the areas of the peaks on the chromatograph trace.

3.5.2 Preparation of the Cement Samples

A stock solution of solvent was made for all the bone cement samples. This contained 0.27ml hexane, to act as an internal standard, in 750ml chlorobenzene. A sample of approximately 0.3g cement was weighed out and the weight recorded accurately. The cement sample was then added to 25ml of the hexane laced solvent and dissolved by gentle warming at 35°C for 12 hours followed by sonication in a water bath at 70°C for 20 minutes. The solutions were then left for 12 hours, to allow the barium sulphate particles to settle out of solution. A 0.4µl sample of each

cement solution was injected into the chromatograph, and the relative peak areas from the trace were recorded. Approximately six injections of each cement solution were run to obtain a mean and standard deviation for the results.

The residual monomer contents of both fully cured and normal bone cement samples were analysed immediately after curing and after storage in the various environments used for the fracture tests.

3.5.3 Calibration of the Equipment

The areas of the peaks on the chromatograph trace, are related to the amounts of the chemicals present in the sample which was injected. A calibration graph of the ratios of the peak areas of internal standard (hexane) to monomer versus the ratios of the weights of these two chemicals in the solution was plotted. Several calibration solutions were prepared containing known weights of both hexane and methylmethacrylate monomer in chlorobenzene, to give weight ratios around those expected from the cement samples. The calibration solutions were then injected into the chromatograph, and the peak areas for the hexane and the monomer recorded. Six injections of each calibration solution were run to obtain a mean value and the standard deviation.

3.5.4 Calculation of Residual Monomer Content

The peak area ratios of hexane to monomer from the chromatograph traces for the polymer solutions were converted to weight ratios using the calibration graph. The mass of hexane in the 25ml cement solution was calculated by converting the known volume present in the stock solvent into a weight using its density. Thus knowing the weight ratio of hexane to monomer and the actual weight of hexane present in the solution, the weight of monomer in the cement solutions could be evaluated. The weight of monomer was then converted into a percentage residual monomer content for that particular cement sample. Measurements of the residual monomer content of the cement were accurate to $\pm 0.1\%$.

3.6 Method for Molecular Mass Determinations

A summary of the experimental technique used to determined the molecular mass of the cement is presented in Appendix A.

3.6.1 Details of the Equipment

The molecular mass of the PMMA component of the bone cement was determined using a Bruker LC21 gel permeation chromatograph (GPC) in association with a LC41 data station. Three 5μm PL Gel columns with exclusion limits of 10^4, 10^3 and 500Å were used with differential refractive index detection. The eluent was tetrahydrofuran at a flow rate of $1cm^3/min$.

3.6.2 Preparation of the Cement Samples

Approximately 0.25g of the cement sample was weighed out and the mass recorded accurately. The sample of cement was then dissolved in 50ml of tetrahydrofuran by gentle warming at 35°C for 12 hours followed by further heating in an oven at 55°C for 6 hours. The solutions were then left for 12 hours, to allow the barium sulphate particles to settle out of solution. The polymer-tetrahydrofuran solutions were kept in a light proof box to prevent degradation of the polymer by ultra violet light. Injections of 50μl of the 5% (w/v) PMMA solutions were made, and the chromatograms recorded. As this was a preliminary study only one injection of each cement solution was run, to see if any trends could be identified.

The molecular mass of samples of normal and fully cured cement was evaluated both immediately after curing and after long-term storage in the same environments as those used for the fracture tests.

3.6.3 Calibration of the Equipment

Eight polymethylmethacrylate (PMMA) standards of known molecular mass, ranging from $2x10^3$ to 10^6 were used to calibrate the columns. The samples of PMMA were dissolved in tetrahydrofuran to make a 5% (w/v) solution. A 50ml sample of this solution was then injected into the chromatograph, and the chromatograms recorded. Thus a calibration graph of molecular mass versus retention time was obtained.

3.6.4 Calculation of Molecular Masses

The LC41 data station software uses the calibration graph to convert the retention times into molecular masses, and to obtain plots of the amount of material versus its molecular mass. Values of M_w (the weight average molecular mass) and M_n (the number average molecular mass) were also obtained from the LC41 data station. The molecular mass of the samples could be determined to an accuracy of ±5%.

3.7 Microscopy Techniques

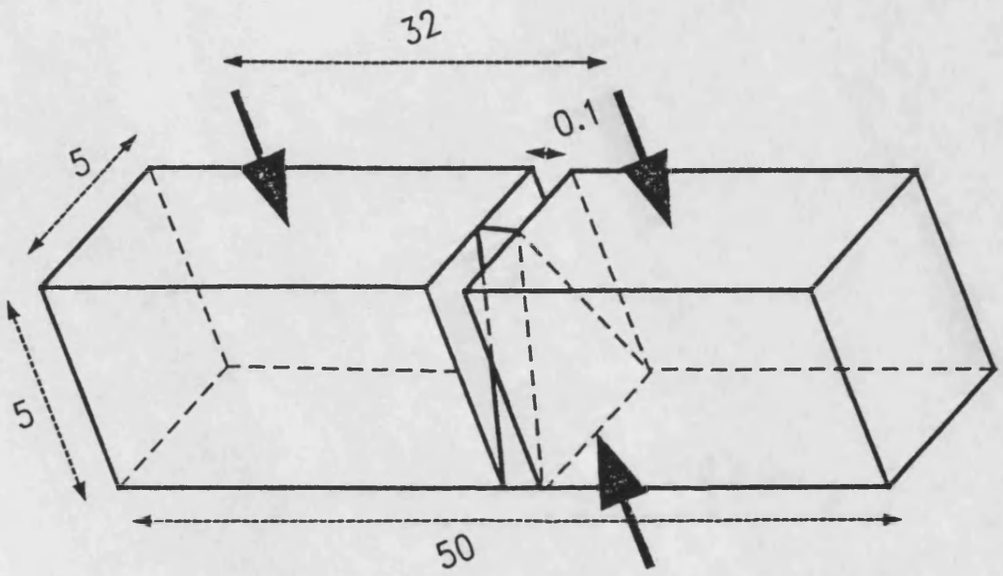
Cement fracture surfaces, samples of the powder component of the cement and polished sections of the cured cement were characterised using scanning electron and optical microscopy techniques. Both these techniques required a certain amount of sample preparation before the specimens could be examined.

Samples of the powder component of the cement and the fracture surfaces of test specimens were examined on a JEOL T-330 scanning electron microscope (SEM). To facilitate electron microscopy of the cement powders, they were mounted onto aluminium stubs using double sided Sellotape and then sputter coated with gold. The surfaces of the fracture specimens were also gold coated, and they were

painted down the side with a carbon paint to provide a conductive path for the electrons.

Samples of cured bone cement were mounted in a cold-curing epoxy resin and when hardened, polished using standard metallographic techniques. The specimens were then etched in concentrated nitric acid, as described by Smith (1961). A Zeiss ICM 405 Light Microscope was then used to examine the cured cement using reflected light and Nomarski Differential Interference Contrast (DIC).

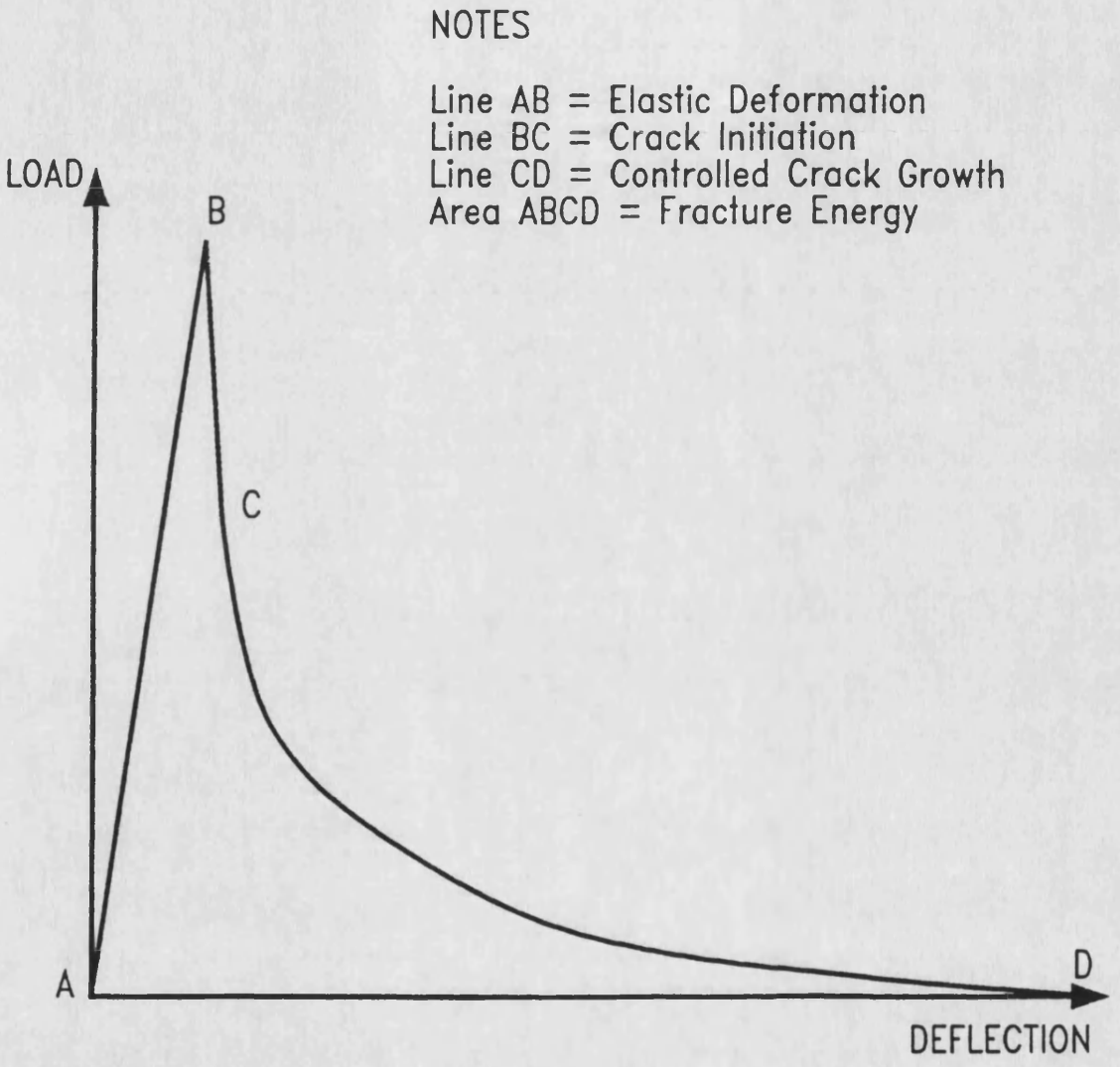
Figure 3.1 : Schematic Diagram of a Test Specimen



NOTES

Diagram is not to scale
All measurements are in mm
Bold arrows indicate loading points

Figure 3.2 : Idealised Load–Displacement Curve



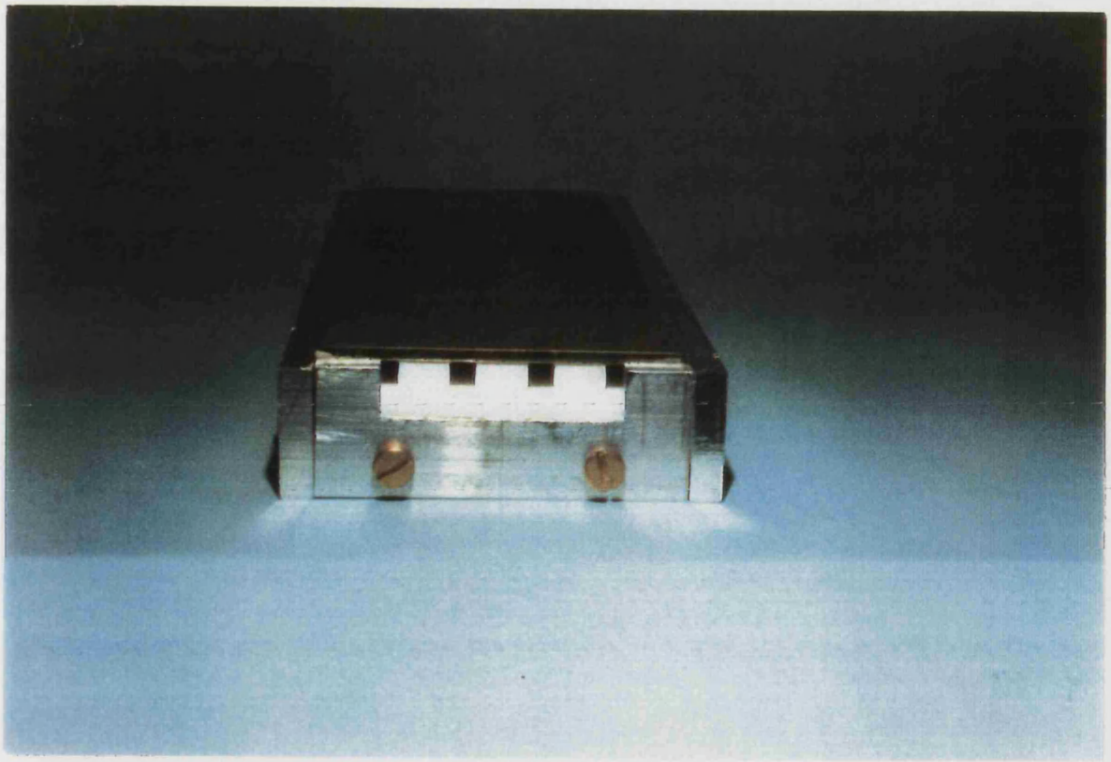


Figure 3.3a : Mould for Producing Work of Fracture Specimens - End View.

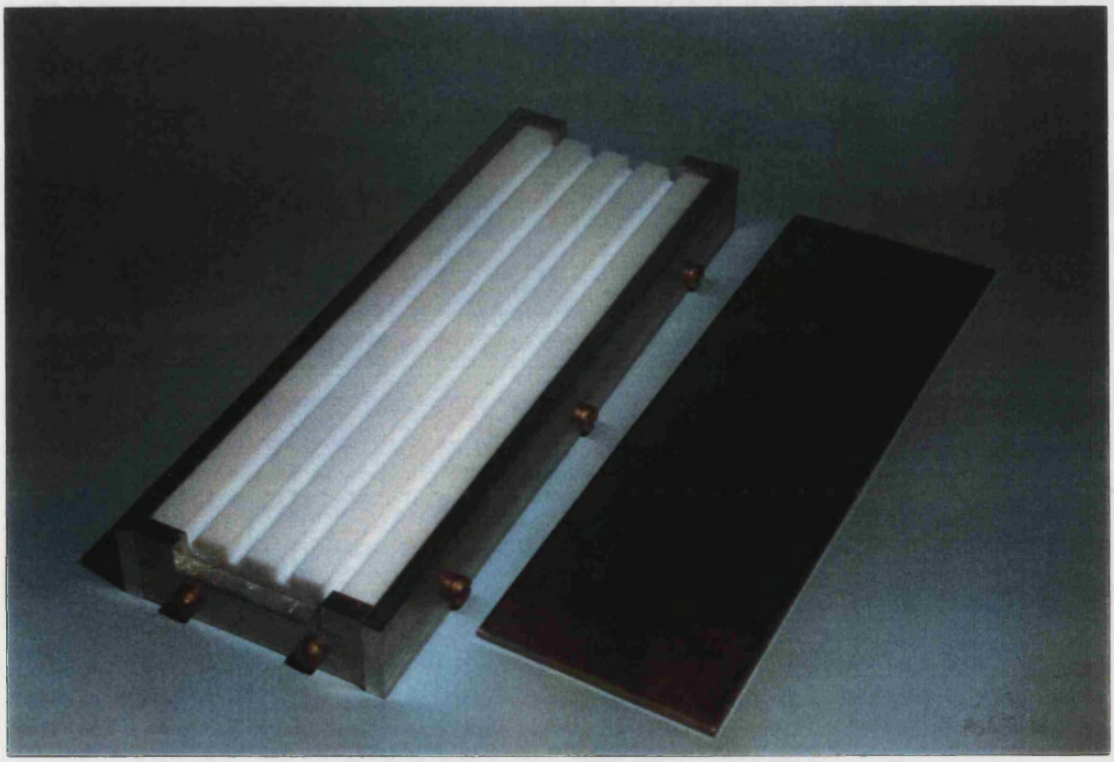


Figure 3.3b : Mould for Producing Work of Fracture Specimens - Top View.

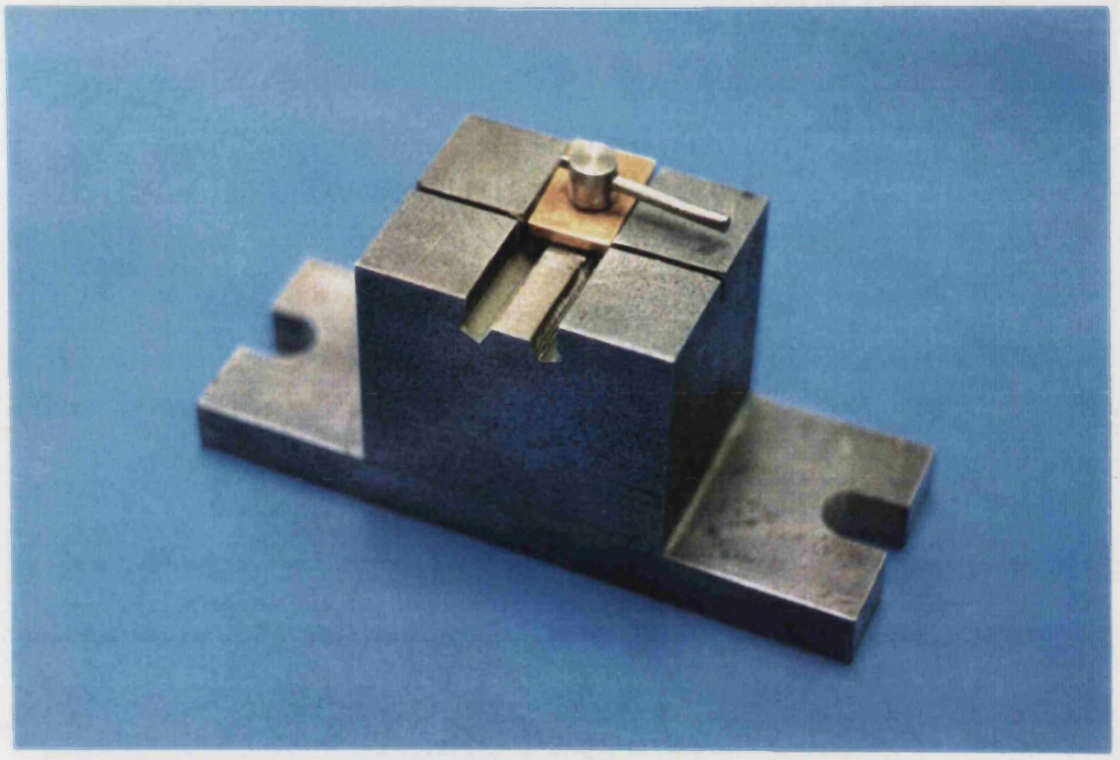


Figure 3.4a : Purpose Made Jig for Notching Work of Fracture Specimens - Top View.

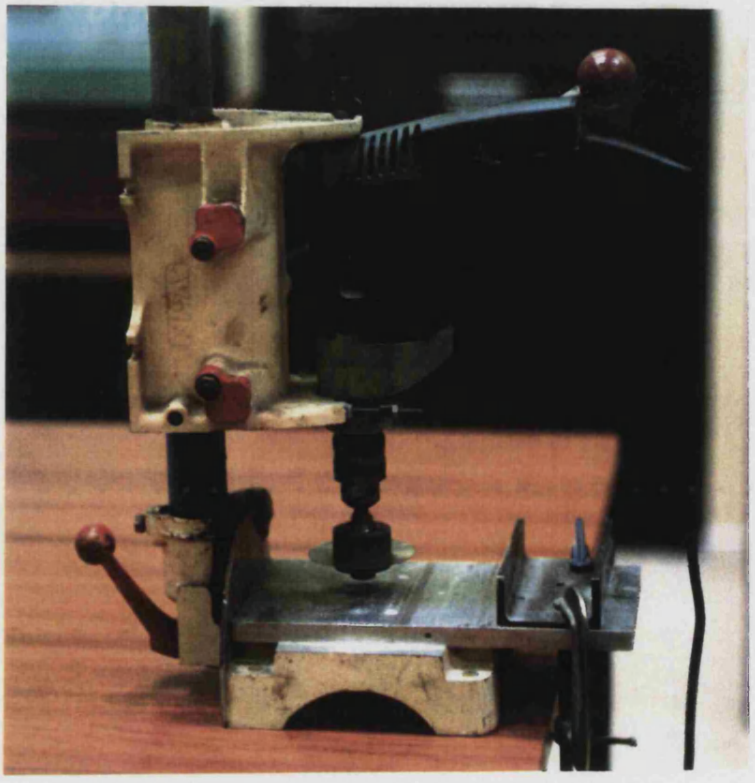


Figure 3.4b : Slitting Saw Arrangement for Notching Work of Fracture Specimens.

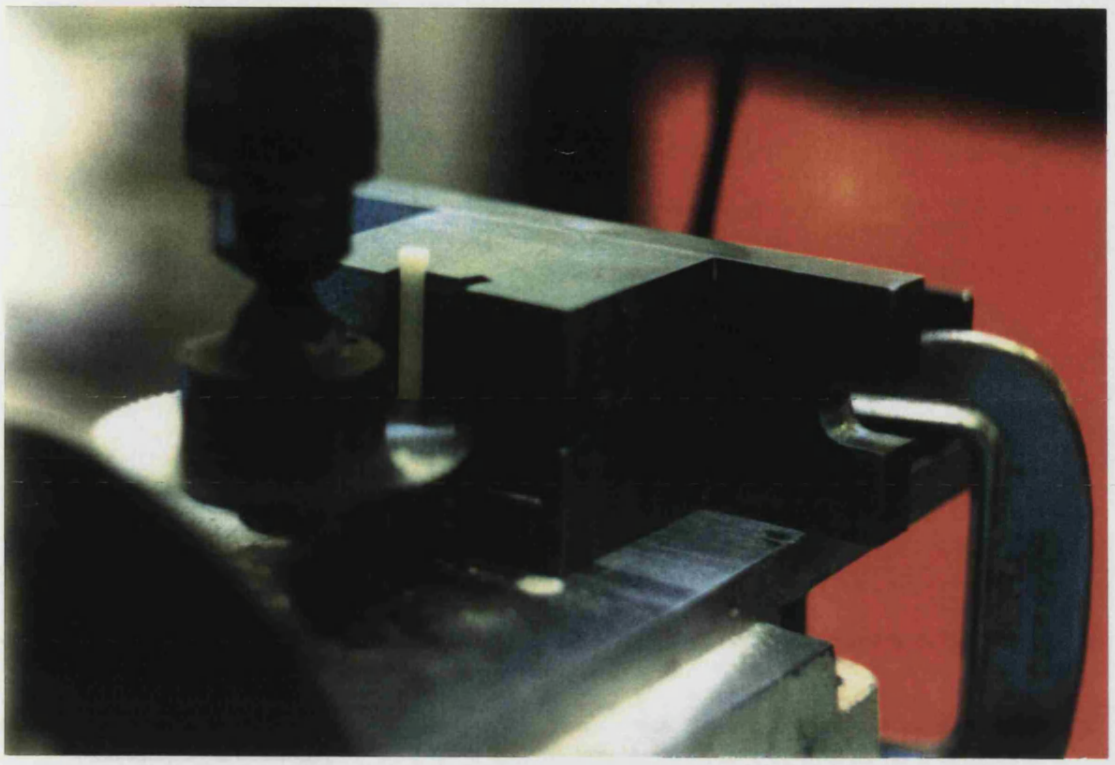


Figure 3.4c : Work of Fracture Specimen Being Notched - Top View.

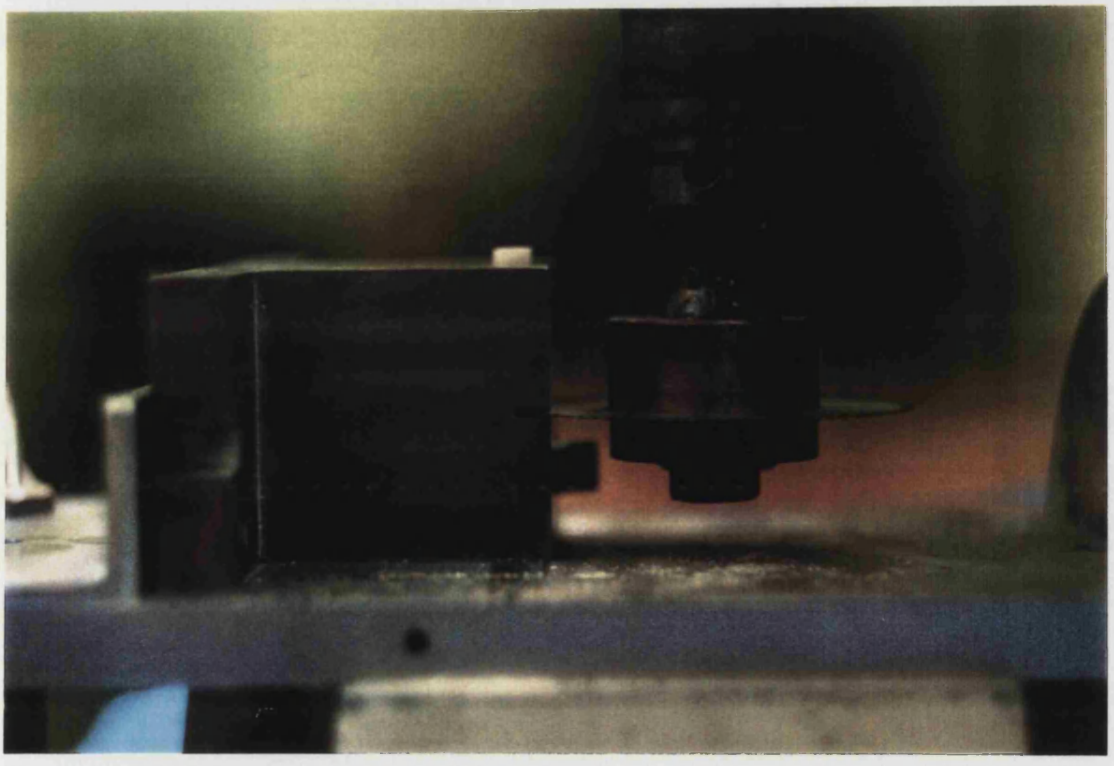


Figure 3.4d : Work of Fracture Specimen Being Notched - Side View.

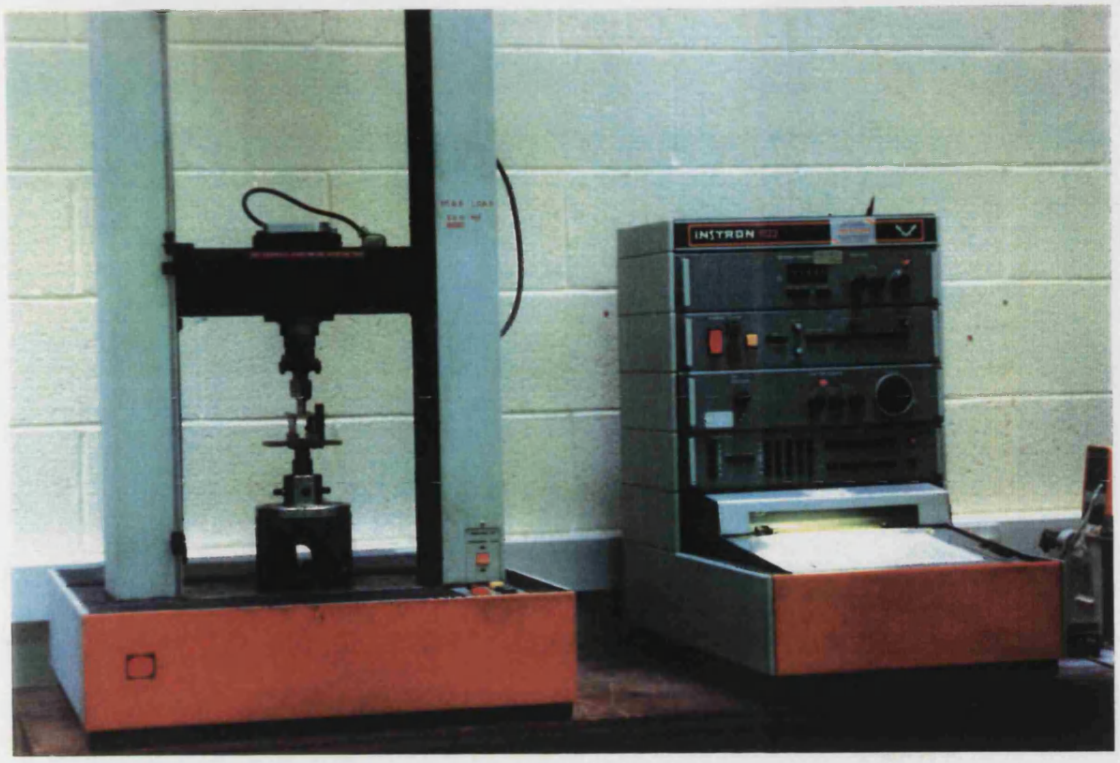


Figure 3.5a : Instron 1122 Testing Machine Used for Testing Work of Fracture Specimens.

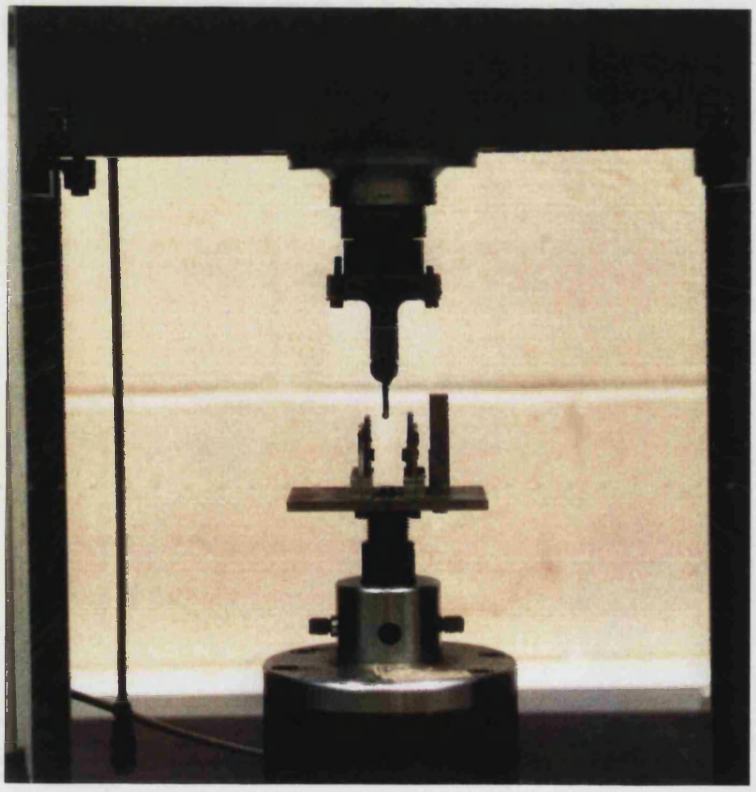


Figure 3.5b : Three Point Bend Equipment Used for Testing Work of Fracture Specimens.

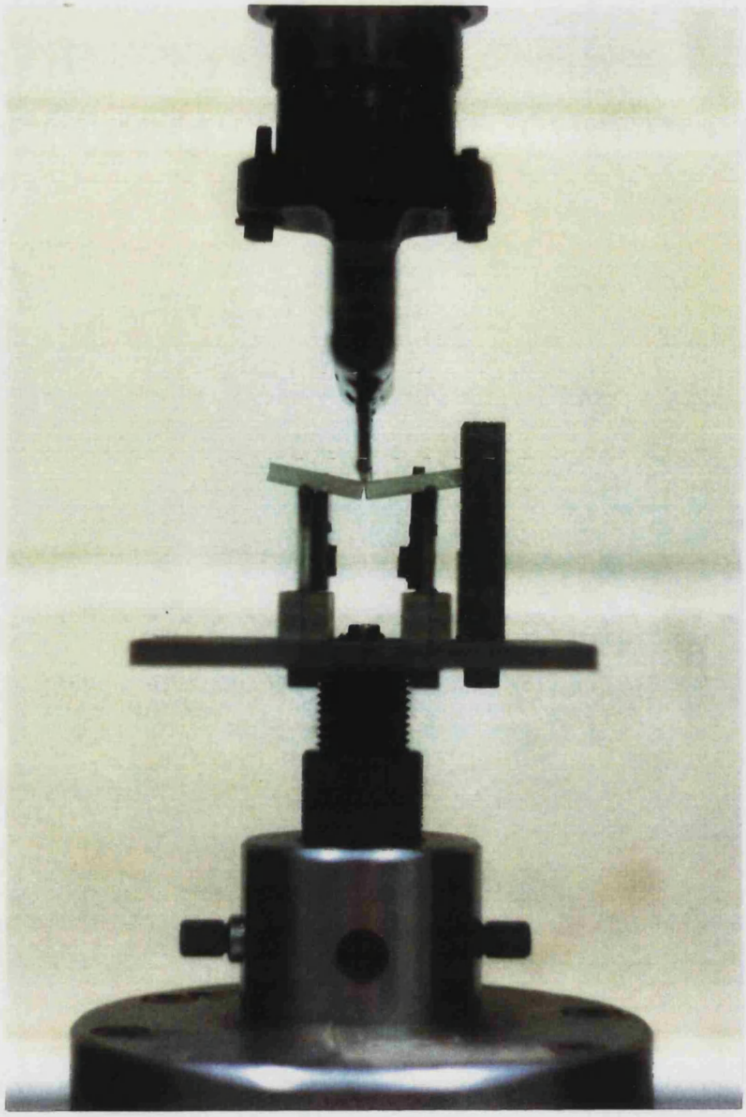


Figure 3.5c : Work of Fracture Specimen Being Tested.

Figure 3.6a : Joyce Loebl Magiscan 2A Image Analyser Used to Measure Fracture Areas.

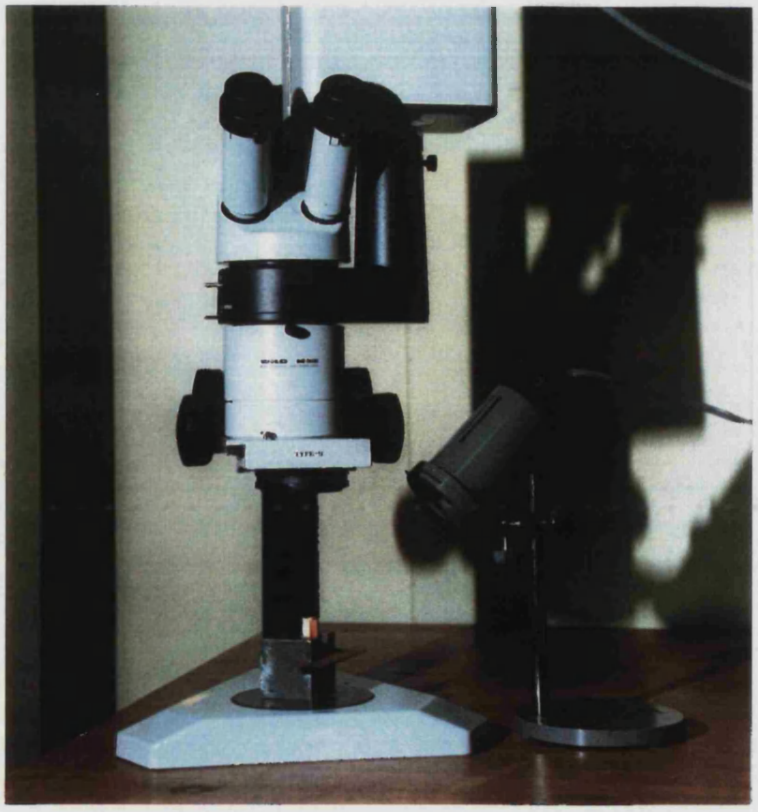


Figure 3.6b : Wild M3Z Optical Microscope with Fracture Specimen and Oblique Lighting Arrangement.

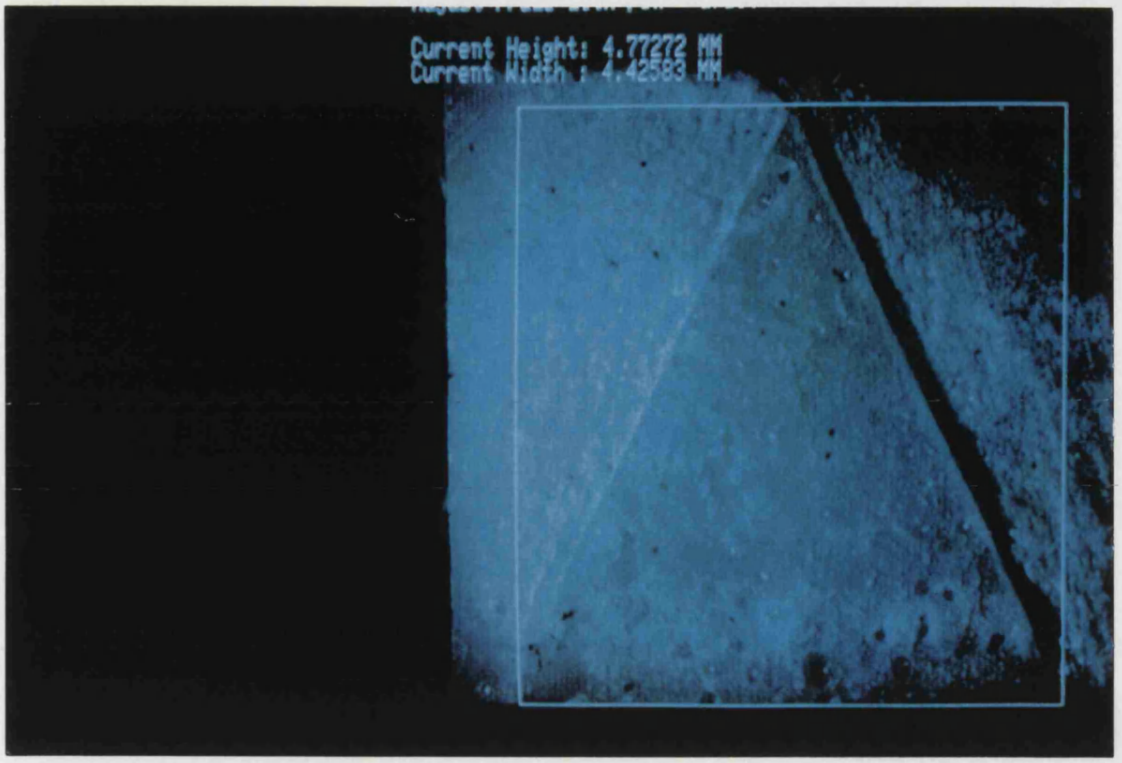


Figure 3.7 : Television Image of a Work of Fracture Specimen Showing the Microscaler Framing the Triangular Fracture Surface.

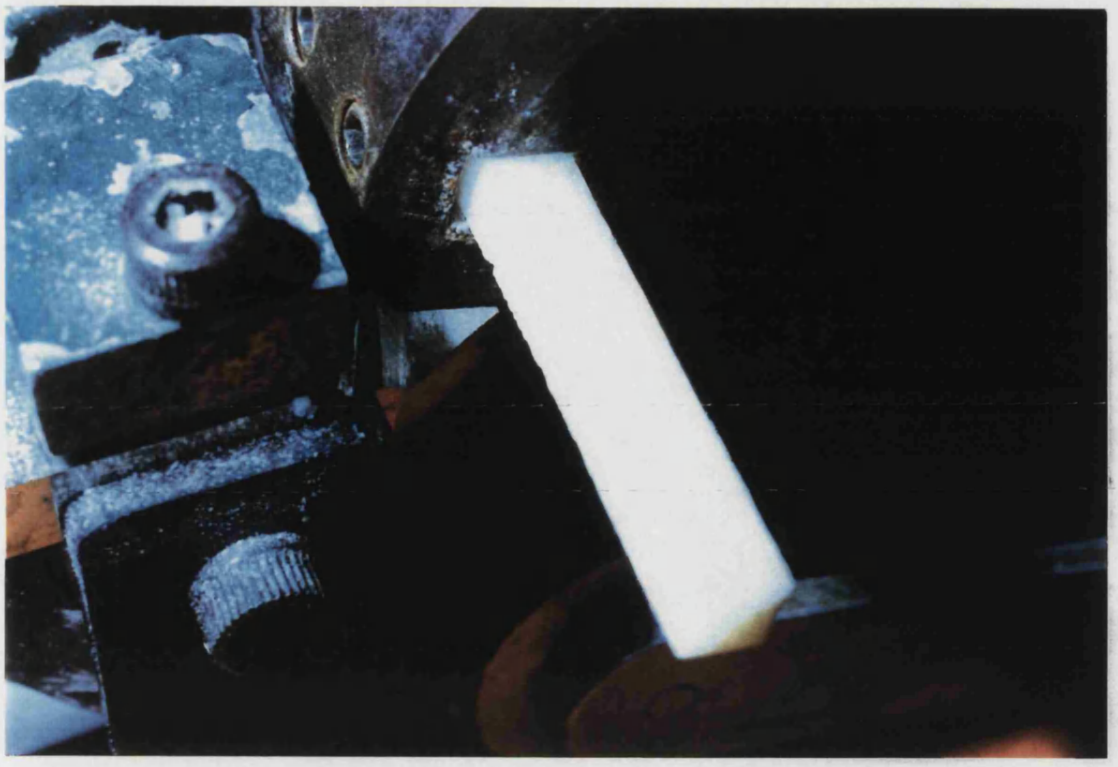


Figure 3.8a : Notching Jig for Rapid Fracture (Impact) Tests - Top View.

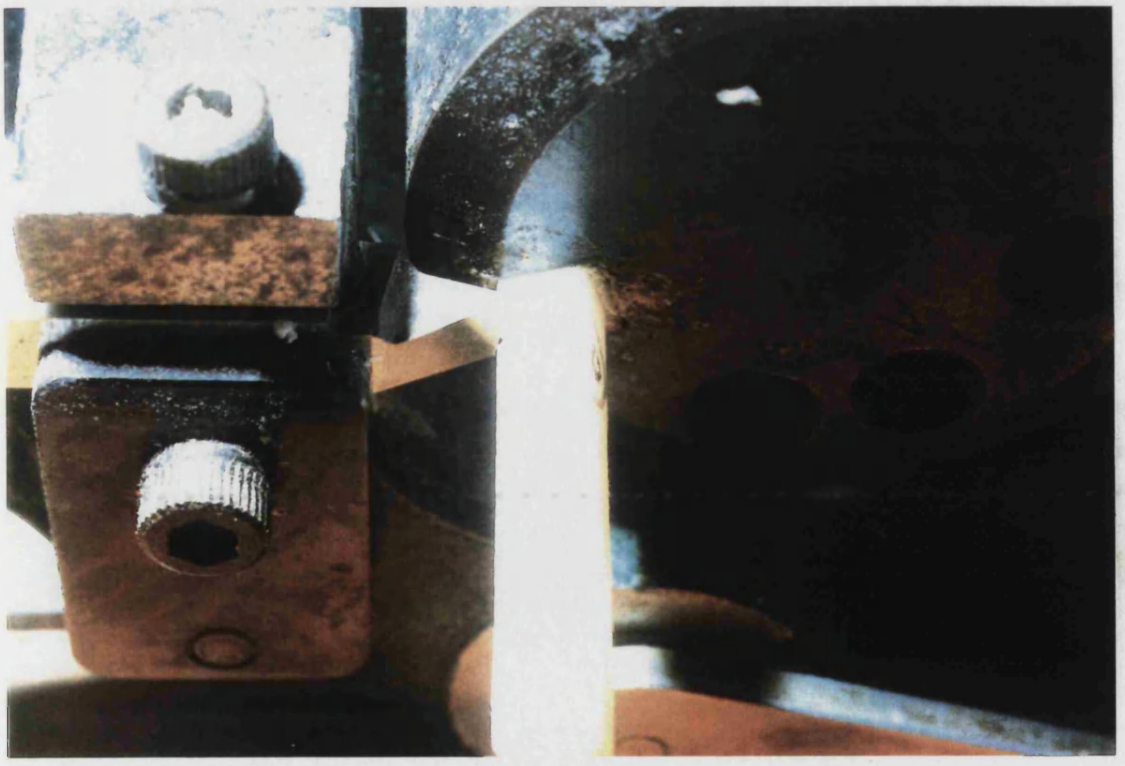


Figure 3.8b : Notching Jig for Rapid Fracture (Impact) Tests - Side View.

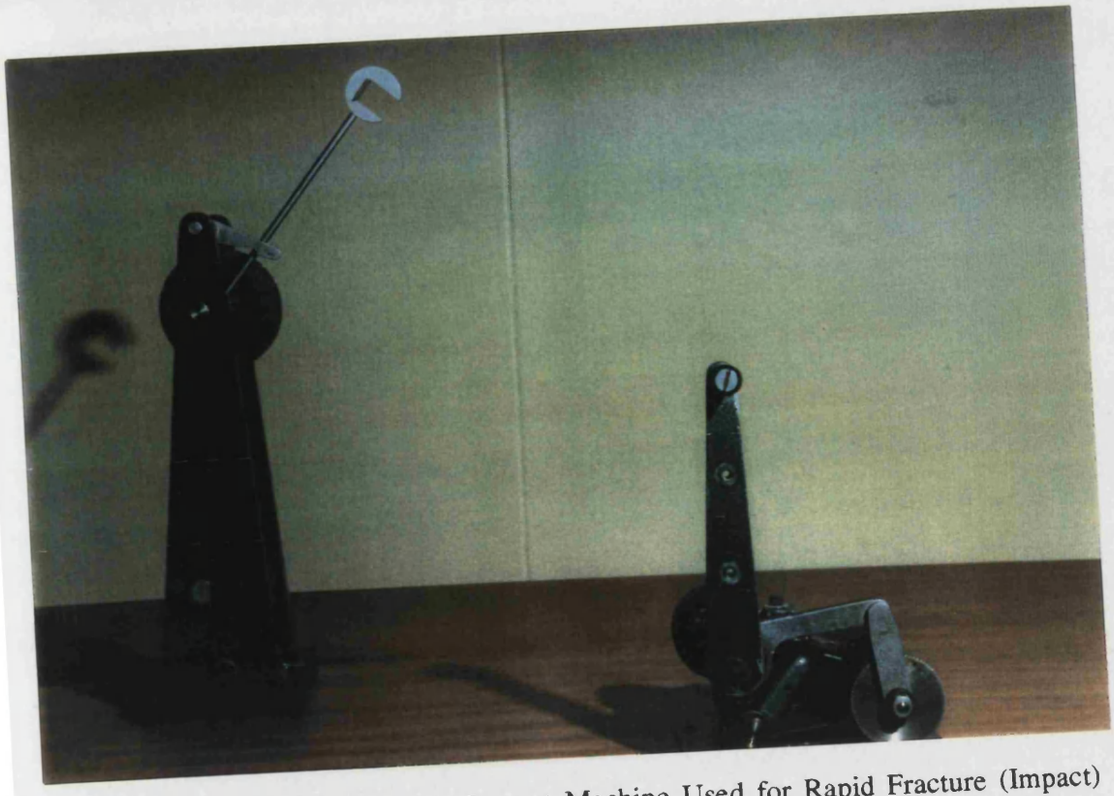


Figure 3.9a : Hounsfield Plastic Impact Machine Used for Rapid Fracture (Impact) Tests - Side View.

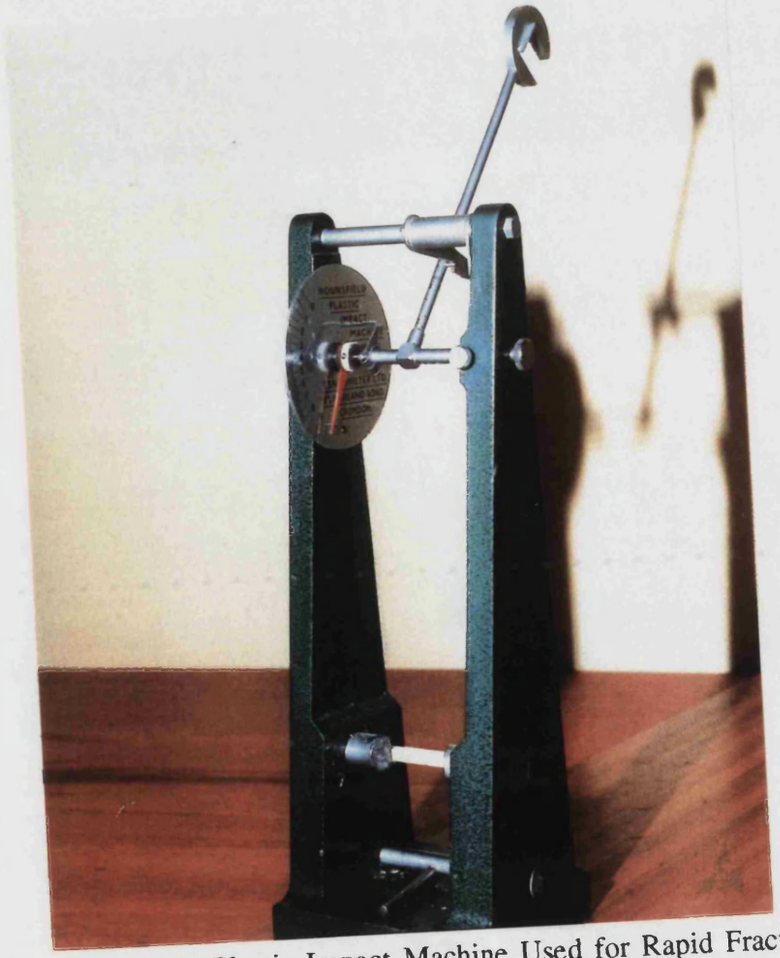


Figure 3.9b : Hounsfield Plastic Impact Machine Used for Rapid Fracture (Impact) Tests - Front View.

Figure 3.9c : Hounsfield Plastic Impact Machine Used for Rapid Fracture (Impact) Tests - Specimen Being Tested.

4. WORK OF FRACTURE

4.1 Work of Fracture Results

4.1.1 Details of the Presentation of the Results

Although 12 - 13 samples from each of the eight environments were tested for every storage period, not all these results were used in calculating the mean work of fracture (WOF). If the fracture surface of a sample contained more than 20% porosity, for example if there was a large void in the sample, an abnormally low WOF value was obtained. This value was considered to be unrepresentative as the void acted as a structural defect masking any effects of storage in the various environments on the mechanical behaviour of the cement. Thus these results were disregarded as also suggested by Bargar, Brown, Paul, Voegli, Hseih and Sharkey (1986). Samples which contained these large voids were easily identified from their load - displacement curves, a typical example of which is shown in Figure 4.1. The failure mode of these specimens was catastrophic due to the very high stress concentrations induced by the voids, and the subsequent WOF value was a reflection of the effect of the voids rather than of the ingress of the storage media - the object of this investigation.

In the tables of results the column headed "number of samples" refers to the number of usable results obtained and does not include any unrepresentative specimens. The tables also give the mean WOF value, standard deviation, and 95% confidence interval (95%CI) for both normal and fully cured cement samples at every storage period in each of the eight storage media.

The WOF results are also plotted graphically on sixteen separate graphs, eight showing the results for samples of normal cement and a further eight showing those for fully cured cement. Figures 4.2 - 4.17 all have the WOF plotted on the y-axis and storage time shown on the x-axis. The standard deviations are not shown on any of the graphs to allow easier comparison of the data, but the statistical significance of the results is discussed in Appendix C.

The first set of four bar charts (Figures 4.2 - 4.5, and 4.12 - 4.15) show the average WOF values for each storage period in the four different media. Each figure corresponds to one of the storage media and shows the WOF results for both storage temperatures. The bars represent the average WOF values for the two temperatures at each storage period. These graphs allowed the general effects of storage in the four media on the WOF to be identified. They also allowed the WOF results for the two storage temperatures to be compared.

The second set of two bar charts show the WOF results for each of the two storage temperatures, with the results for the four different media shown on each graph (see Figures 4.6 and 4.7, and 4.14 and 4.15). The bars represent the average WOF values for each of the storage media at the various storage periods. These bar charts allowed the comparison of the WOF results for the four different storage media.

The final set of two graphs (Figures 4.8 and 4.9, and 4.16 and 4.17) contain the same information as the previous two, but are plotted as x-y graphs with the x-axis as a true time axis. The symbols represent the average WOF values for the four storage media at each of the storage periods. These two graphs allowed the effect of storage time in the various environments to be studied.

4.1.2 Results for Normal Cement

The WOF results for bone cement samples prepared in the normal manner are presented in Tables 4.1 - 4.8. The mean WOF values are also shown graphically in Figures 4.2 - 4.9.

Figures 4.2 - 4.5 show the WOF results for specimens stored in air, water, Ringer's, and lipid respectively. It can be seen from Figure 4.2 that the WOF for samples stored in air decreased with storage time. Whereas Figures 4.3 - 4.5 show that for specimens stored in the fluid media the WOF increased with storage time. From Figures 4.2 - 4.5

it can also be seen that in all four of the storage media, the WOF for samples stored at 21°C was consistently higher than for samples stored at 37°C.

Figures 4.6 and 4.7 show the WOF results for specimens stored at 21°C and 37°C respectively. From these bar charts it can be seen that there was no apparent difference between the WOF results for samples stored in water and those stored in Ringer's. The two bar charts also showed that the WOF for lipid stored samples was consistently lower than that for the two water based media.

In Figures 4.8 and 4.9 the WOF results are plotted on a true time x-axis for samples stored at 21°C and 37°C respectively. From these graphs it can be seen that for all eight storage environments the most dramatic changes in WOF occurred within the first few days of storage. For samples stored in air at 21°C the decrease in WOF was a gradual one, over a 200 day storage period, with little change in the WOF after 200 days. Samples stored in air at 37°C had a much more dramatic decrease in WOF, the greatest reduction occurring within the first 7 days and there being little change after this. For samples stored in the fluid media at both 21°C and 37°C the most dramatic increases in WOF occurred within the first 80 days. At longer storage periods (up to 500 days) the WOF continued to gradually increase, although less dramatically. After samples had been stored in the fluids at 21°C for periods greater than 500 days there appeared to be little change in the WOF with time. However, for the same length of storage, samples stored at 37°C in water and Ringer's appeared to experience a decrease in WOF.

4.1.3 Results for Fully Cured Cement

The WOF results for samples of fully cured bone cement are presented in Tables 4.9 - 4.16. The mean WOF values are also shown graphically in Figures 4.10 - 4.17.

Figures 4.10 - 4.13 show the WOF results for specimens stored in air, water, Ringer's, and lipid respectively. From Figure 4.10 it can be seen that for samples stored in air, there was no change in the WOF over the 500 day time period studied. Although the bar charts show that samples stored in air at 37°C generally tended to have a lower WOF than those stored at 21°C, this difference was only slight. Figures 4.11 - 4.13 show that in the fluid media there was a dramatic increase in WOF with storage time. From these bar charts it can be seen that the maximum WOF values were reached at 84 days for samples stored at both 21°C and 37°C. The WOF for the samples stored at 21°C then remained steady until 497 days storage when there was a decrease in the WOF. In contrast the WOF of samples stored at 37°C reached a peak at 84 days, with a decrease at 182 days to a then steady value which remained steady until the maximum storage period of 497 days. The bar charts also show that for storage times up to 21 days in the three fluid media, the WOF was higher for samples stored at 37°C than for those stored at 21°C. After 84 days storage, however, there was a change over and samples stored at 21°C had a higher WOF than those at 37°C. By 497 days samples stored at both temperatures had similar WOF values.

Figures 4.14 and 4.15 show the WOF results for samples stored at 21°C and 37°C respectively. It can be seen from these graphs that storage of samples in the fluid media resulted in a significant increase in the WOF when compared with samples stored in air. As with the samples of normal cement, specimens stored in water and Ringer's had similar WOF values at each of the time periods studied. Also similar to the results for normal cement, storage of fully cured samples in lipid gave consistently lower WOF values than for the two water based media.

The WOF results for samples stored at 21°C and 37°C are shown on a true time x-axis in Figures 4.16 and 4.17. These graphs show that for samples stored at both 21°C and 37°C in air there was no change in the WOF with storage time. For samples stored in the fluid media at both temperatures there was an increase in WOF followed by a

decrease at long storage periods. The graphs show that the most significant changes in WOF occurred within the first few days of storage (up to 21 days). The variation in WOF with longer storage periods was shown to be much more gradual.

4.1.4 Effect of Porosity on WOF

As discussed in section 3.2, the WOF samples have a triangular cross section. Due to the infinitely high stress concentrations at the apex of this triangle, a crack is initiated at a load much lower than the failure strength of the cement. Once the crack is initiated it is prevented from propagating through the entire sample in a catastrophic manner due to the increasing cross sectional area throughout the sample. Hence complete catastrophic failure of the WOF test specimens does not occur. Instead the crack, once initiated, propagates through the remaining cross section in a controlled manner due to the constant cross head speed. A typical example of a load-displacement curve for a pore free sample is shown in Figure 4.18.

In an idealised sample as the crack was initiated it propagated through only a very small area of the triangular cross section. On the load-displacement curve this crack initiation was associated with a sudden decrease in load, see region BC in Figure 3.2. The load-displacement curve then decayed in an exponential manner, as the constant speed of the cross head forced the crack to propagate through the remaining cross section (region CD in Figure 3.2).

If a sample contained a large void (greater than 2mm in diameter), as mentioned in section 4.1.1, then the load-displacement curve resembled the one shown in Figure 4.1. These samples had a lower peak load as the void acted as a crack nucleation site, thus reducing the crack initiation energy. This also reduced the WOF value for that particular sample. The presence of the void led to the sample being less rigid and more compliant, hence structural deformation of the sample would occur as well as crack

propagation. The overall effect of a large void in the plane of fracture was to act as a structural defect, and artificially weaken the sample of cement.

If the sample contained a small pore (less than 1mm in diameter) then the load-displacement curve resembled the one shown in Figure 4.19. These small pores acted as crack blunters causing the crack to deviate around them. A small blip corresponding to the crack deviating around a small pore can be seen on the load-displacement curve in Figure 4.19. This blip increased the crack propagation energy slightly, although not substantially. Hence samples containing one or two small pores were still included in the study despite the small irregularities shown on the load-displacement curves.

4.1.5 Effect of Laboratory Testing Temperature on WOF

The WOF for samples of normal and fully cured cement evaluated at two different laboratory temperatures, 0°C and 40°C are presented in Tables 45 and 46. The mean WOF values for both types of cement at the two testing temperatures are also shown as a bar chart in Figure 4.20.

From Figure 4.20 it can be seen that, for normal cement, there was a significant increase in the WOF with an increase in laboratory testing temperature from 0°C to 40°C (see Appendix C). With fully cured cement, however, this increase, although statistically significant, was not as dramatic.

There were also differences in the load-displacement curves for tests performed at the two different temperatures. Figures 4.21 - 4.24 show the load-displacement curves for samples of both types of cement at the two testing temperatures.

4.1.6 Effect of Notching Before Storage on WOF

The WOF results for samples of normal and fully cured cement samples which were notched before and after storage in water at 21°C for 6 weeks are presented in Tables 47 and 48. The mean WOF values for the pre-notched and control samples are also shown as a bar chart in Figure 4.25.

It can be seen from Figure 4.25 that for both normal and fully cured cement, the WOF for samples which were notched prior to storage was significantly higher than for those notched after storage (see Appendix C).

4.2 Discussion of the Work of Fracture

As the specimens were fractured within 5-10 minutes after being removed from their storage environment it is unlikely that any significant desorption would have occurred, Therefore the chemical and physical conditions inside the specimens at fracture would have been similar to those whilst the specimen was in the storage environment (Kusy, 1978). *In vivo*, however, the cement would actually fail in the presence of the body fluids which may have an increased plasticising effect on the crack tip. Beaumont (1976) reported that diffusion of saline or blood to a moving crack tip had no effect on the rate of crack growth in bone cement. However, Benbow (1961) showed that if the crack tip of a specimen of industrial PMMA is in intimate contact with water, then the fracture energy is increased by a factor of four. This was, however, when wet samples were compared with dry samples. Therefore a much smaller (if any) increase in the fracture energy would be expected if the WOF were tested with the crack tip in contact with the storage environments.

4.2.1 Normal Cement

When comparing the mechanical properties of bone cements to those of acrylic dental resins it must be remembered that many dental acrylics are cross-linked whereas bone cements are not. This will make the polymer network of dental resins more rigid than those of bone cements, resulting in a higher elastic modulus for dental resins compared with bone cements.

4.2.1.1 Effect of Storage in Air

It was shown in section 4.1.2 that the WOF of samples stored in air decreased over the 2 year time period studied. This decrease was attributed to the loss of residual monomer, which is known to act as a plasticiser on the cement.

The plasticising effect of residual monomer on polymethylmethacrylate has been reported by many authors (Smith and Bains, 1956, Kusy, 1978, and Caul, Sweeney and Paffenbarger, 1956), the latter of whom showed a direct relationship between residual monomer content and elastic modulus of dental acrylics.

It has been reported (Smith and Bains, 1956) that both the physical and mechanical properties of dental acrylics change as the time of cure is increased. The strength, hardness, and density all increase, whereas the ductility decreases with length of cure. These changes become smaller with time, and the authors suggested that they were associated with the degree of polymerisation and the reduction of the residual monomer content. Scheerer, Swartz, Norman and Phillips (1964) reported that the rate of improvement of the Young's modulus, yield strength and hardness of dental acrylic resins had a direct relationship with the decrease in the residual monomer content. Brauer, Termini and Dickson (1977) showed a linear dependence of the indentation resistance on the amount of residual monomer present in samples of cured bone cement. The above results all suggest that as residual monomer is lost from within the cement its ductility decreases and the elastic modulus increases. As the cement

becomes more brittle one would expect the WOF to also decrease, as is indicated from the results of this study.

Holm (1977) observed an increase in the Young's modulus of bone cement during the first week after mixing. It has been shown by Lee, Ling and Wrighton (1973) that residual monomer is lost from the cement during mixing due to evaporation. The authors also suggested that observed increases in compressive strength over the first week after mixing were due to further losses of monomer after polymerisation. This supports our theory that evaporation of residual monomer from the cement does occur after polymerisation. As discussed above, the result is a reduction in the elastic modulus of the cement, which in turn leads to a lower WOF value.

4.2.1.2 Effect of Storage in Water and Ringer's

Section 4.1.2 showed that the effect of storing samples in water was to increase the WOF with time. This increase was attributed to the plasticising effect of the ingress of water on the cement. There was no significant difference between the WOF values for water and those for Ringer's. So the physiological salts appeared to have no effect on the fracture behaviour of bone cement. The increase in WOF was due solely to the plasticising effect of the ingress of the water.

Several authors have commented on the plasticising effect of the ingress of water into bone cement (Wang and Pilliar, 1989a, and Watson, Miles and Clift, 1991). Lautenschlager, Stupp and Keller (1984) wrote that "when located within the interior of the acrylic structure, H_2O acts as a plasticizer, increasing molecular mobility within the cement, thereby allowing more deformation to occur. Water may also inhibit crack growth at defect boundaries and dissipate stresses throughout the bulk material."

There has been only one other study which has looked at the influence of the storage environment on the WOF of bone cement (Watson, Miles and Clift, 1990), and the

results of this study compared well with our results. In general both the mean WOF values and the experimental variability of the study by Watson *et al* (1990) were greater than those obtained in this thesis. However, both studies showed similar trends for the influence of the environment on the WOF. It was shown that storage in water resulted in a higher WOF than storage in air, and that storage in both environments at 37°C led to a lower WOF than storage at 21°C.

Johnson and Jones (1991) showed that storage and testing of bone cement specimens in water at 37°C as opposed to in air at 23°C resulted in an increase in the fracture toughness, K_{IC}. The authors found a 50% increase in K_{IC} for bulk polymerised samples of 100% methylmethacrylate monomer. However, these samples were heat treated to yield residual monomer contents of less than 1% and were also pore free. Hence direct comparison with the results of this study is not possible, but it interesting to note the similarity of the trends observed in the two studies.

Wright, Sullivan and Arnoczky (1984) reported a significant increase in the fracture toughness of cement which had been stored in Ringer's lactate for 2 months compared with zero-time control samples. The authors also found a similar increase in the fracture toughness for cement which had been implanted subcutaneously in dogs for 2 months. Frietag and Cannon (1976) showed that specimens which were cured at 37°C in bovine serum had a higher fracture toughness than those which were cured in air. These studies appear to support the results of this study, that cement which is stored in fluid media has a higher WOF than cement which is stored in air. Frietag and Cannon (1976) attributed this increase in fracture resistance to the storage fluid having a plasticising effect on the cement, which improved the resistance to crack propagation.

Although the majority of papers concerned with the effect of the environment on the fracture behaviour of cement support this thesis, Jaffe, Rose and Radin (1974) in their study found the effects of storage for up to 2 years in bovine serum at 37°C on the

static properties and the compressive fatigue behaviour of bone cement to be negligible. Wang and Pilliar (1989a) reported that the fracture toughness of cement after storage in water will depend upon the relative amounts of absorbed water and residual monomer present in cement. The authors also suggested that the ingress of water can have both positive and in some cases a detrimental effect on K_{IC}, as discussed in section 2.8.

4.2.1.3 Effect of Storage in Lipid

It was shown in section 4.1.2 that the effect of storage in lipid was again to increase the WOF values, although not as significantly as the two water based media. One would expect the lipid to be a stronger plasticiser of polymers than water, however, this was not the case with bone cement. It is known that the monomer is a powerful lipid solvent (Howmedica, 1989) and it is thought that this monomer-lipid interaction was responsible for the WOF values being lower than expected.

Only two papers (Ferracane, 1981, and Perkins, Lee and Ling, 1990) have looked at the effect of fat on the mechanical properties of bone cement, and yet it is well known that there is a high fat content in the bone cavity which is generated during joint replacement. Ferracane (1981) suggested that the incorporation of fatty bone marrow into the bone cement was responsible for the observed decreases in the mechanical properties in clinical situations. The author showed that increasing percentages of fat incorporated into the cement resulted in decreases in the tensile and compressive strengths of the material; when 50% (by weight) of fat was incorporated into the cement the compressive strength decreased by 65%. This decrease in strength was attributed to the formation of fat laminations within the cement mass. Perkins *et al* (1990) using Intralipid and normal saline as test media, reported that the creep rate of bone cement was higher in hydrated samples than in dry specimens. The work of Perkins *et al* (1990) supports the findings of this thesis that both Ringer's and Intralipid had a plasticising effect on bone cement.

4.2.1.4 Effect of Storage Temperature

It was found in section 4.1.2 that in all four storage environments the WOF for samples stored at 37°C was lower than for those stored at 21°C. This result was not as expected. It was thought that the higher temperature would increase the diffusion and mobility of the storage media and thus increase the environmental ingress, which would in turn increase the WOF. However, the higher temperature may also have increased the diffusion and mobility of the residual monomer, thus making it easier for the monomer to either leach into the storage medium, or for continued curing to occur. Thus there would appear to be some competition between environmental ingress and residual monomer content. The results of this study indicate that at 37°C the increased mobility of the monomer had a greater overall effect on the WOF than increased mobility of the storage media.

Watson, Miles and Clift (1990) found similar results to those in this study, that with storage in both air and water, samples which were stored at 37°C had a lower WOF than those stored at 21°C.

Haas, Brauer and Dickson (1975) showed that regardless of polymerisation temperature, samples which were aged at 37°C for several hours had lower indentation and higher recovery values than those aged at 21°C for a similar time. This would suggest that samples aged at 37°C have a higher modulus and hence a lower resistance to crack growth than samples aged at 21°C, which supports the results obtained in this thesis.

4.2.1.5 Long-term Storage

It was shown in section 4.1.2 that for samples stored in the two water based media at 37°C, there was a significant decrease in WOF after storage for 2 years. There also appeared to be a non-significant decrease in the WOF for samples stored at 21°C.

Rostoker, Lereim and Galante (1979) implanted specimens of a similar geometry to ours into rabbit muscle immediately after they had polymerised. After implantation for periods of 6, 12 and 24 months the fracture stress was evaluated in air using three point loading. The authors found a non-significant increase in the fracture stress in the first 12 months, and a significant decrease between 12 and 24 months. These results were in very good agreement with the findings of this study, but the authors offered no explanation for their trends.

It has been reported that PMMA is susceptible to environmental stress cracking in certain environments (Davidson, Lynch and Locke, 1988). Although this could be offered as an explanation for the deterioration in the long-term mechanical properties of bone cement *in vivo*, it does not explain the long-term decrease in the WOF observed in this thesis. The specimens used in this thesis were not stored under load, therefore the only stresses which could be present within our samples would be residual stresses due to the contraction of the cement on setting. Also the study by Davidson *et al* (1988) showed that the environmental stress cracking susceptibility of PMMA was greater in lipid and fatty environments than it was in Ringer's solution. In this thesis, however, it appeared that the long-term decrease in the WOF was significantly greater for the two water based media than for the lipid solution. Therefore, it is unlikely that environmental stress cracking is responsible for the long-term deterioration the WOF observed in this thesis.

4.2.2 Fully Cured Cement

Section 4.1.3 showed that the WOF for fully cured specimens tested immediately after heat treatment was significantly lower than that for normal samples tested 30 minutes after curing. This was attributed to the removal of virtually all the residual monomer from within the fully cured cement mass.

It has been shown by Smith and Bains (1956) that dental acrylics which were cured at room temperature had a higher residual monomer content than those which had been cured by boiling. The authors also found that the cold-cure acrylics had a greater flexibility and lower strength compared to the boiling cured acrylics. This was attributed to the higher monomer content of the former samples. The study by Smith and Bains (1956) supports our hypothesis that the heat treatment of the fully cured samples led to a lower residual monomer content compared to samples of normal cement, which in turn resulted in an increase in elastic modulus and hence a lower WOF for the fully cured material.

Storage of fully cured samples in the fluid media was shown (see section 4.1.3) to have the same plasticising as that observed with the normal cement. However, it was found with fully cured cement, that the discrepancy between the WOF for lipid stored samples and that for water stored samples was smaller than it was for samples of normal cement. This has been attributed to the elimination of the residual monomer as a variable from within the cement. Therefore the effect of the monomer-lipid interaction, which was observed with the normal cement, would not occur with the fully cured material. Hence for the fully cured cement, the effect of storage in lipid would be similar to that of storage in water and Ringer's.

For storage periods up to 3 months, it was found that samples of fully cured cement which were stored in the fluid media at 37°C had higher WOF values than samples which were stored at 21°C. This was the reverse of the effect observed with the

normal cement, where the samples stored at 37°C had the lower WOF. It is postulated that since the residual monomer had been removed from the fully cured cement, there was no longer a competition between increased monomer loss and increased environmental ingress at the elevated storage temperature. The only effect of storage at 37°C as opposed to 21°C, was to increase the environmental ingress into the fully cured cement, thus increasing the WOF.

With longer storage periods (over 3 months) there was a significant decrease in the WOF which occurred earlier for samples stored at 37°C than for samples stored at 21°C. This decrease in WOF occurred after 182 days and 497 days for samples stored at 37°C and 21°C respectively. The same effect was seen to a lesser, yet still significant, extent in the normal material after storage for 749 days at both 21°C and 37°C. These long-term decreases in the WOF could be due to a process termed physical aging (Struik, 1978).

Summarising Struik's theory for physical aging :

PMMA is a glassy polymer, which is essentially a solidified supercooled liquid. The free volume (V_f) of the material is therefore greater than it would be at equilibrium. As the material is cooled from above its glass transition temperature (T_g) to room temperature, the free volume decreases, but remains greater than the equilibrium value. Physical aging involves the continued slow decrease of the free volume towards the equilibrium value. As the free volume decreases, so the polymer chain mobility also decreases, and the material becomes more brittle. The rate of physical aging increases with elevated aging temperatures, and is also related to the thermal history of the polymer. Since the fully cured material was heated beyond its glass transition temperature (115°C) for over 15 hours, and the normal material only reached the temperature of the polymerisation exotherm (approximately 100°C) for several minutes, it is likely that the fully cured material would be more susceptible to physical aging than the normal material. Storage of the cement at 37°C as opposed to 21°C

would also increase the rate of physical aging, thus the cement stored at the higher temperature would exhibit brittle tendencies earlier than the cement stored at 21°C. The WOF results from this thesis support both these hypotheses, thus physical aging of the cement is offered as an explanation of the deterioration in the WOF after long-term storage in the fluid media. This effect was not observed with the air stored cement as it failed in a completely brittle manner. Using impact tests, Struik (1978) has shown when PMMA fails in a brittle manner, changes in the free volume have no effect on the impact strength of the material. If, however, the material fails in a ductile manner (by increasing the test temperature), then physical aging and free volume changes once again become important.

4.2.3 Effect of Porosity

Although it has been shown by many authors that porosity can have a detrimental effect on the mechanical properties of bone cements (Black, 1988, DeWijn, Slooff and Driessens, 1975, and Bayne, Lautenschlager, Compere and Wildes, 1975), the results of this study (see section 4.1.4) indicate that the WOF test is very forgiving of small porosity contents. It was shown that small pores have little effect on the WOF, and that it is only large voids (which act more as structural defects than as an aspect of the material's properties) which cause a significant reduction in the WOF.

There have been conflicting studies on the effect of porosity on the fracture properties of bone cements. Rimnac, Wright and McGill (1986) and Wang and Pilliar (1989a) found that the fracture toughness of bone cement was not dependant on the porosity content. However, Beaumont and Young (1975) reported that K_{IC} was dependant on void content, and DeWijn, Slooff and Driessens (1975) found that porosity led to a reduction in the impact strength of cement. There has also been evidence of cracks emanating from pores within the cement *in vivo* (Gharpuray, Keer and Lewis, 1990).

One possible explanation for the discrepancies in the above studies is that the fracture behaviour of the cement depends more on the porosity size distribution than on the actual porosity content. The results of this study suggest that if there are several small pores within the cement, their effect on the fracture resistance will be negligible. Whereas if the same percentage of porosity was found in one large void, then there would be a significant reduction in the resistance to crack growth of the material. It is also possible that the relationship between fracture toughness and porosity content is sensitive to the particular test method used.

4.2.4 Effect of Laboratory Testing Temperature

From section 4.1.5 it was found that there was an increase in the WOF with elevated testing temperatures. This would be consistent with a decrease in the elastic modulus of the cement with the higher laboratory temperature.

Lee, Ling and Vangala (1977) observed decreases in the Youngs modulus (4%) and the compressive strength (10%) of samples of bone cement when tested at 37°C as opposed to 21°C. Holm (1977) also reported a decrease in the elastic modulus of bone cement when tested at body temperature as opposed to laboratory temperature. These results support our observed increase in the WOF with an increase in testing temperature, which is not surprising as PMMA bone cement is a visco-elastic material.

4.2.5 Effect of Pre-notching

Section 4.1.6 showed that samples which were notched before storage in water had a significantly higher WOF than samples which were notched immediately prior to testing. This could be due to one of two reasons. Firstly pre-notching may allow greater penetration of the fluid into the notched region of the cement. Secondly notching prior to storage may cause plasticisation of crack tip. Although both of these possibilities would have a significant influence on the fracture behaviour of the

cement, the trends observed in the WOF with storage in the various environments would not be altered.

4.3 Summary of the Work of Fracture

This study has shown that the WOF test procedure devised by Tattersall and Tappin was effective in identifying changes in the fracture behaviour of bone cement. Conventional fracture tests tend to be sensitive to porosity within the cement. However, the Tattersall-Tappin test is much more forgiving and small pores do not significantly influence the WOF values. Large voids, which do have a significant effect on the WOF, can be easily identified (and eliminated) due to the shape of the load displacement curve. Thus, in this thesis, the influence of the ageing environment on the WOF was not masked by other variables. In addition, Topoleski, Ducheyne and Cuckler (1990) showed that the fracture surfaces of cement which had failed *in vivo*, laboratory fatigue fracture surfaces and surfaces which failed by slow controlled crack growth were all similar. Hence it was concluded that the fracture micromechanisms which operated in the three situations were the same. Therefore the conditions which influence the WOF are also likely to influence the behaviour of the cement in a fatigue situation and *in vivo*.

This study has helped our understanding of the complexity of the interactions which occur *in vivo*. It has been shown that the individual storage media and temperatures have significantly different effects on the fracture of behaviour of bone cement. In particular, specimens stored in the fluid media behaved in a more ductile manner than those stored in air, and specimens stored at 37°C behaved in a more brittle manner than those stored at 21°C.

A significant decrease in the WOF was observed in this study, with long-term storage of cement in the fluid media. Although a deterioration in the long-term mechanical properties of cement was thought to exist *in vivo*, this thesis is the first study to report such a finding in the laboratory. Clearly this has major clinical significance, particularly in relation to the long-term performance of cement *in vivo*, and may be one explanation for the high incidence of late aseptic loosening of TJR.

The results of this study also have clinical implications with a respect to the rehabilitation of patients. It was shown that there was an initial increase in WOF due to fluid absorption, which stabilised after 3 months. This would suggest that it may be beneficial for patients to be put on non-weight bearing activities for first few weeks immediately after a joint replacement operation. Haas, Brauer and Dickson (1975) have also suggested that it is "important to minimise the stresses on the joint replacement system during the early post-insertion period", as they found that cement, even when polymerised and stored at 37°C required nearly 24 hours to attain steady state mechanical properties.

Finally, there have been many previous studies which have attempted to characterise bone cement. Most of these, however, have been performed under laboratory conditions. This study has shown that the physiological environment has a significant effect on the mechanical behaviour of cement. It is therefore essential that the laboratory testing conditions replicate the *in vivo* situation as closely as possible.

Table 4.1 : WOF Results for Normal Bone Cement Samples Stored in Air 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
Initial	20	461	30	461±14
1 day	11	423	27	423±18
3 days	10	436	23	436±16
7 days	12	407	45	407±29
21 days	10	373	25	373±18
42 days	11	405	19	405±13
84 days	10	381	20	381±14
217 days	14	350	24	350±14
364 days	11	350	29	350±19
553 days	12	388	35	388±22
749 days	12	363	17	363±11

Table 4.2 : WOF Results for Normal Bone Cement Samples Stored in Air 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	12	341	32	341±20
3 days	11	352	20	352±13
7 days	13	311	29	311±18
21 days	10	305	34	305±24
42 days	11	305	23	305±15
84 days	11	301	12	301±8
217 days	11	240	15	240±10
364 days	11	288	29	288±19
553 days	12	295	19	295±12
749 days	12	283	30	283±19

Table 4.3 : WOF Results for Normal Bone Cement Samples Stored in Water 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	11	459	39	459±26
3 days	12	448	39	448±25
7 days	12	472	41	472±26
21 days	10	491	45	491±32
42 days	11	509	38	509±26
84 days	10	534	40	534±29
217 days	10	523	28	523±20
364 days	10	575	35	575±25
553 days	12	619	42	619±27
749 days	12	603	48	603±30

Table 4.4 : WOF Results for Normal Bone Cement Samples Stored in Water 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	12	391	27	391±17
3 days	13	406	40	406±24
7 days	12	422	21	422±13
21 days	10	451	49	451±35
42 days	12	462	28	462±18
84 days	11	504	23	504±15
217 days	11	490	35	490±24
364 days	11	506	26	506±17
553 days	11	579	24	579±16
749 days	12	508	33	508±21

Table 4.5 : WOF Results for Normal Bone Cement Samples Stored in Ringer's 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	11	444	31	444±21
3 days	12	429	42	429±27
7 days	13	445	34	445±21
21 days	11	453	40	453±27
42 days	12	515	44	515±28
84 days	10	526	23	526±16
217 days	12	521	51	521±32
364 days	11	592	33	592±22
553 days	12	584	35	584±22
749 days	12	556	40	556±25

Table 4.6 : WOF Results for Normal Bone Cement Samples Stored in Ringer's 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	11	370	29	370±19
3 days	11	417	32	417±22
7 days	14	448	31	448±18
21 days	10	424	30	424±21
42 days	11	494	38	494±26
84 days	11	470	37	470±25
217 days	11	505	38	505±26
364 days	12	521	43	521±27
553 days	11	560	28	560±19
749 days	11	502	25	502±17

Table 4.7 : WOF Results for Normal Bone Cement Samples Stored in Lipid 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	11	404	21	404±14
3 days	12	406	37	406±24
7 days	13	454	42	454±25
21 days	12	419	31	419±20
42 days	10	512	46	512±33
84 days	11	489	41	489±28
217 days	10	439	26	439±19
364 days	11	487	32	487±22
553 days	11	548	26	548±17
749 days	11	572	36	572±24

Table 4.8 : WOF Results for Normal Bone Cement Samples Stored in Lipid 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
1 day	12	369	35	369±22
3 days	11	387	26	387±17
7 days	15	418	37	418±20
21 days	10	412	16	412±11
42 days	12	457	29	457±18
84 days	11	458	23	458±15
217 days	12	452	40	452±25
364 days	11	442	29	442±19
553 days	12	444	38	444±24
749 days	12	478	21	478±13

Table 4.9 : WOF Results for Fully Cured Bone Cement Samples Stored in Air 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
Initial	12	237	17	237±11
7 days	11	223	13	223±9
21 days	10	273	18	273±13
84 days	12	252	18	252±11
182 days	11	278	16	278±11
357 days	12	225	21	225±13
497 days	11	282	21	282±14

Table 4.10 : WOF Results for Fully Cured Bone Cement Samples Stored in Air 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	12	218	12	218±8
21 days	10	236	17	236±12
84 days	12	241	18	241±11
182 days	11	233	27	233±18
357 days	13	211	18	211±11
497 days	12	212	28	212±18

Table 4.11 : WOF Results for Fully Cured Bone Cement Samples Stored in Water 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	11	278	24	278±16
21 days	16	401	29	401±15
84 days	11	624	40	624±27
182 days	13	612	48	612±29
357 days	10	642	20	642±14
497 days	11	550	19	550±13

Table 4.12 : WOF Results for Fully Cured Bone Cement Samples Stored in Water 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	14	350	25	350±14
21 days	10	493	24	493±17
84 days	11	601	33	601±22
182 days	13	505	39	505±24
357 days	11	527	24	527±16
497 days	12	518	45	518±29

Table 4.13 : WOF Results for Fully Cured Bone Cement Samples Stored in Ringer's 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	11	255	17	255±11
21 days	11	392	42	392±28
84 days	12	609	26	609±17
182 days	11	558	28	558±19
357 days	9	638	49	638±38
497 days	12	520	33	520±21

Table 4.14 : WOF Results for Fully Cured Bone Cement Samples Stored in Ringer's 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	12	348	23	348±15
21 days	12	495	29	495±18
84 days	12	570	29	570±18
182 days	13	513	45	513±27
357 days	12	508	19	508±12
497 days	11	524	26	524±17

Table 4.15 : WOF Results for Fully Cured Bone Cement Samples Stored in Lipid 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	11	245	12	245±8
21 days	12	362	50	362±32
84 days	12	554	40	554±25
182 days	12	553	34	553±22
357 days	10	564	31	564±22
497 days	9	500	58	500±45

Table 4.16 : WOF Results for Fully Cured Bone Cement Samples Stored in Lipid 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	14	341	26	341±15
21 days	10	499	37	499±26
84 days	13	516	33	516±20
182 days	11	480	38	480±26
357 days	12	484	34	484±22
497 days	11	443	31	443±21

Table 4.17 : WOF Results for Normal Bone Cement Samples Tested at Different Temperatures

Testing Temp.	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
0°C	11	225	27	225±18
40°C	12	417	29	417±18

Table 4.18 : WOF Results for Fully Cured Bone Cement Samples Tested at Different Temperatures

Testing Temp.	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
0°C	12	171	22	171±14
40°C	15	219	24	219±13

Table 4.19 : WOF Results for Normal Bone Cement Samples Notched Prior to and After Storage in Water

Storage Condition	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
Control	11	529	26	529±17
Pre-notched	12	656	39	656±25

Table 4.20 : WOF Results for Fully Cured Bone Cement Samples Notched Prior to and After Storage in Water

Storage Condition	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
Control	11	500	25	500±17
Pre-notched	12	608	44	608±28

Figure 4.1 : Load-Displacement Curve
for a Sample Containing a Large Void

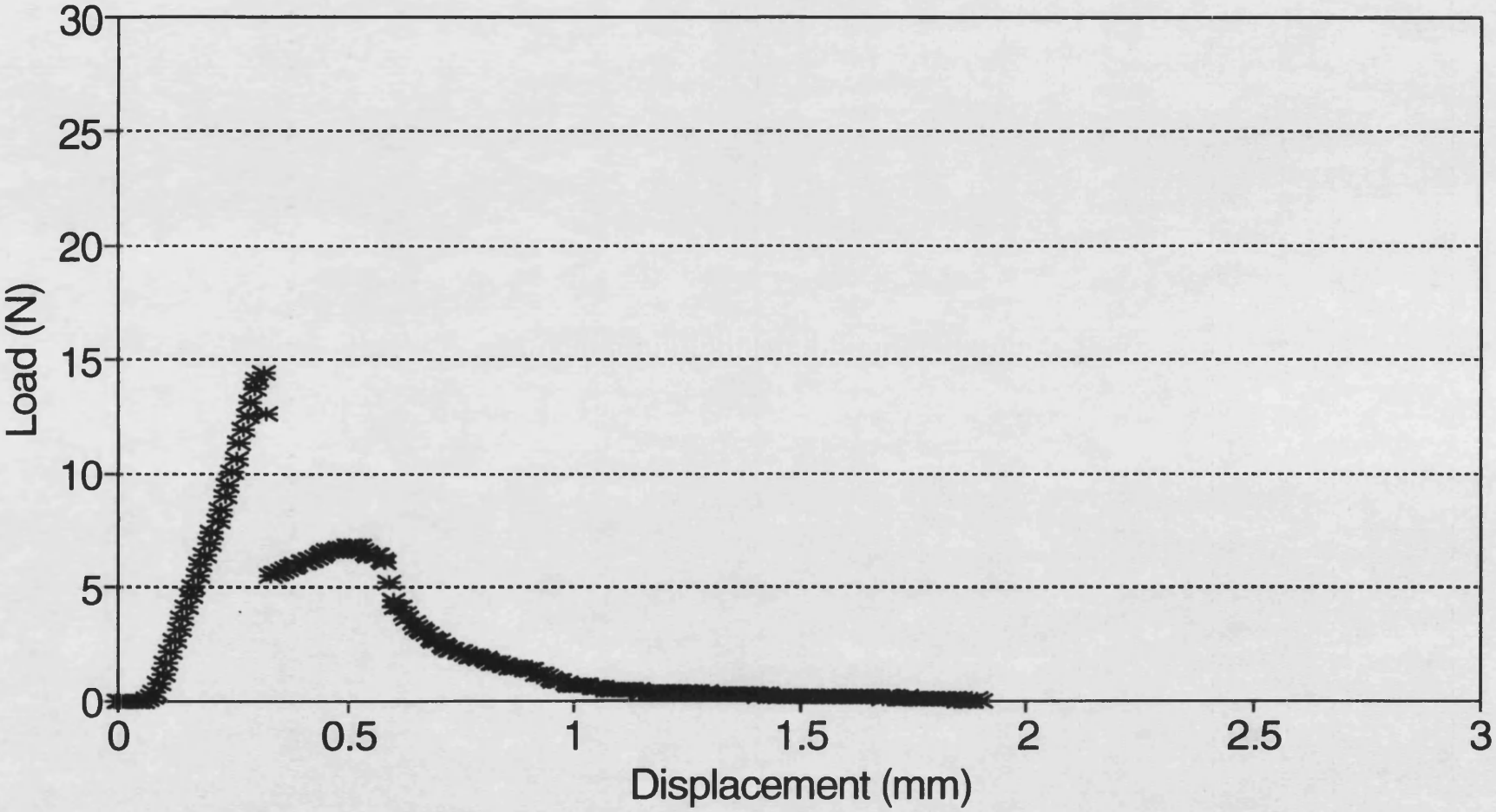


Figure 4.2 : WOF Results for
Normal Cement in Air

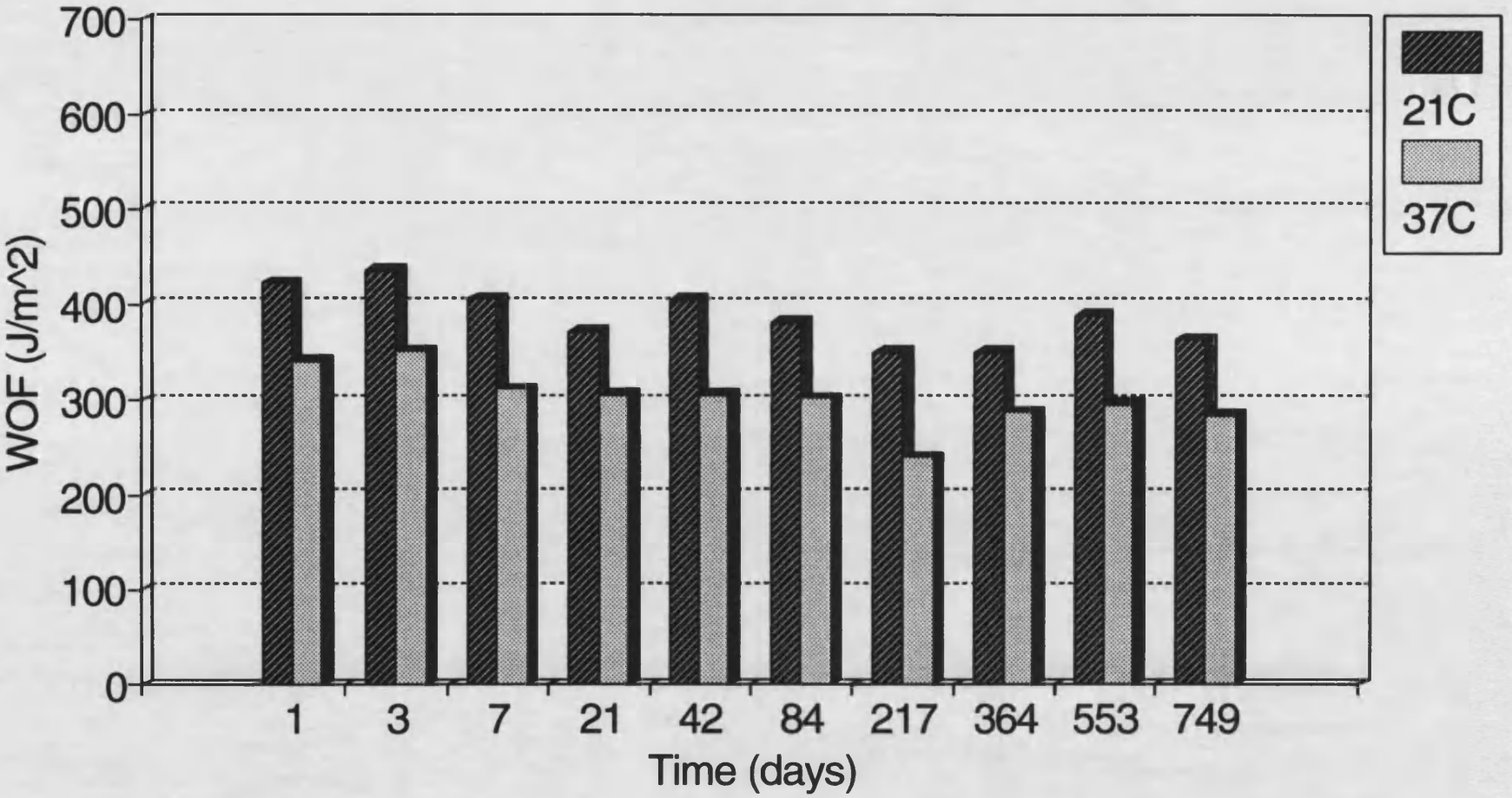


Figure 4.3 : WOF Results for
Normal Cement in Water

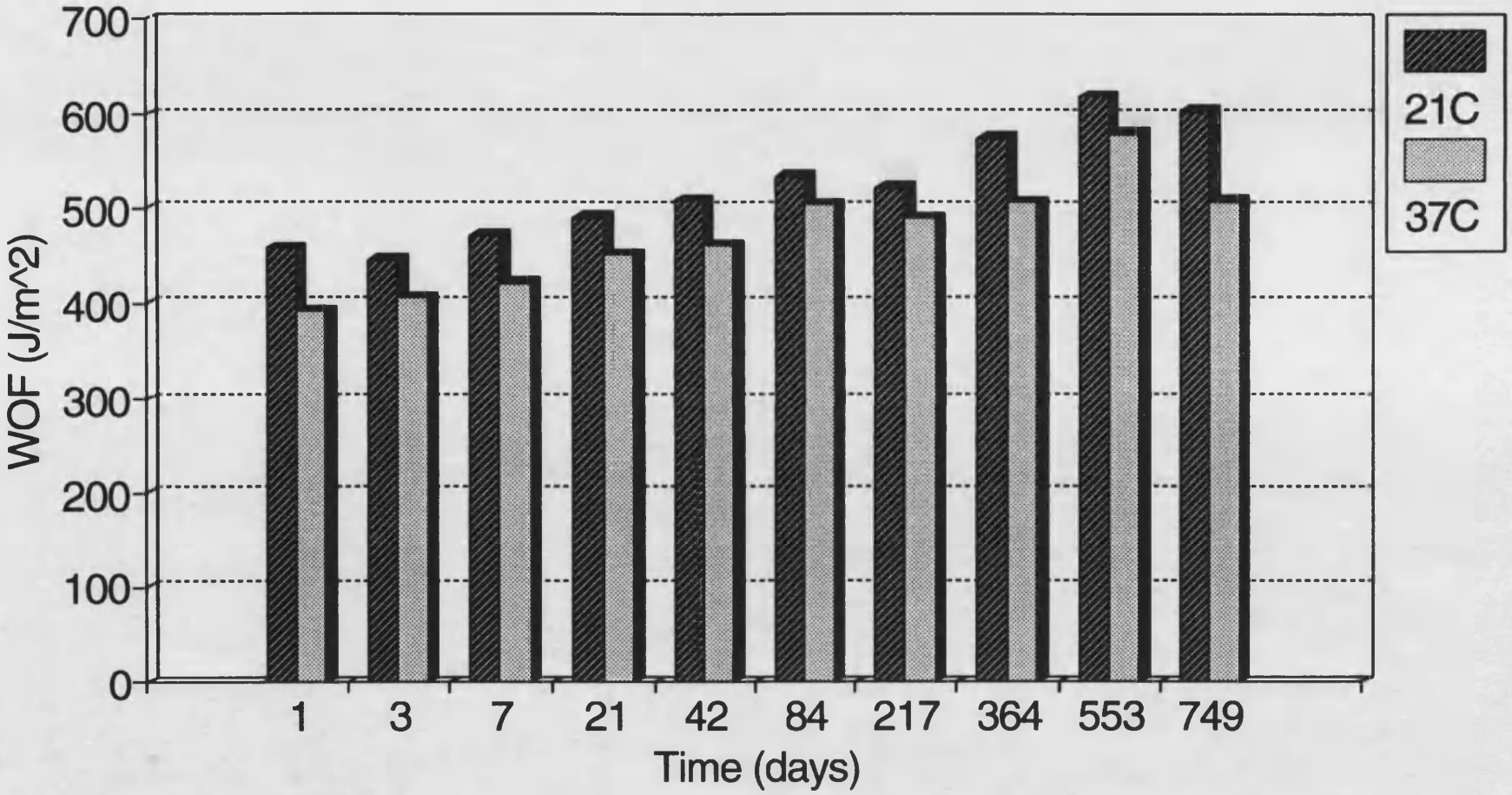


Figure 4.4 : WOF Results for
Normal Cement in Ringer's

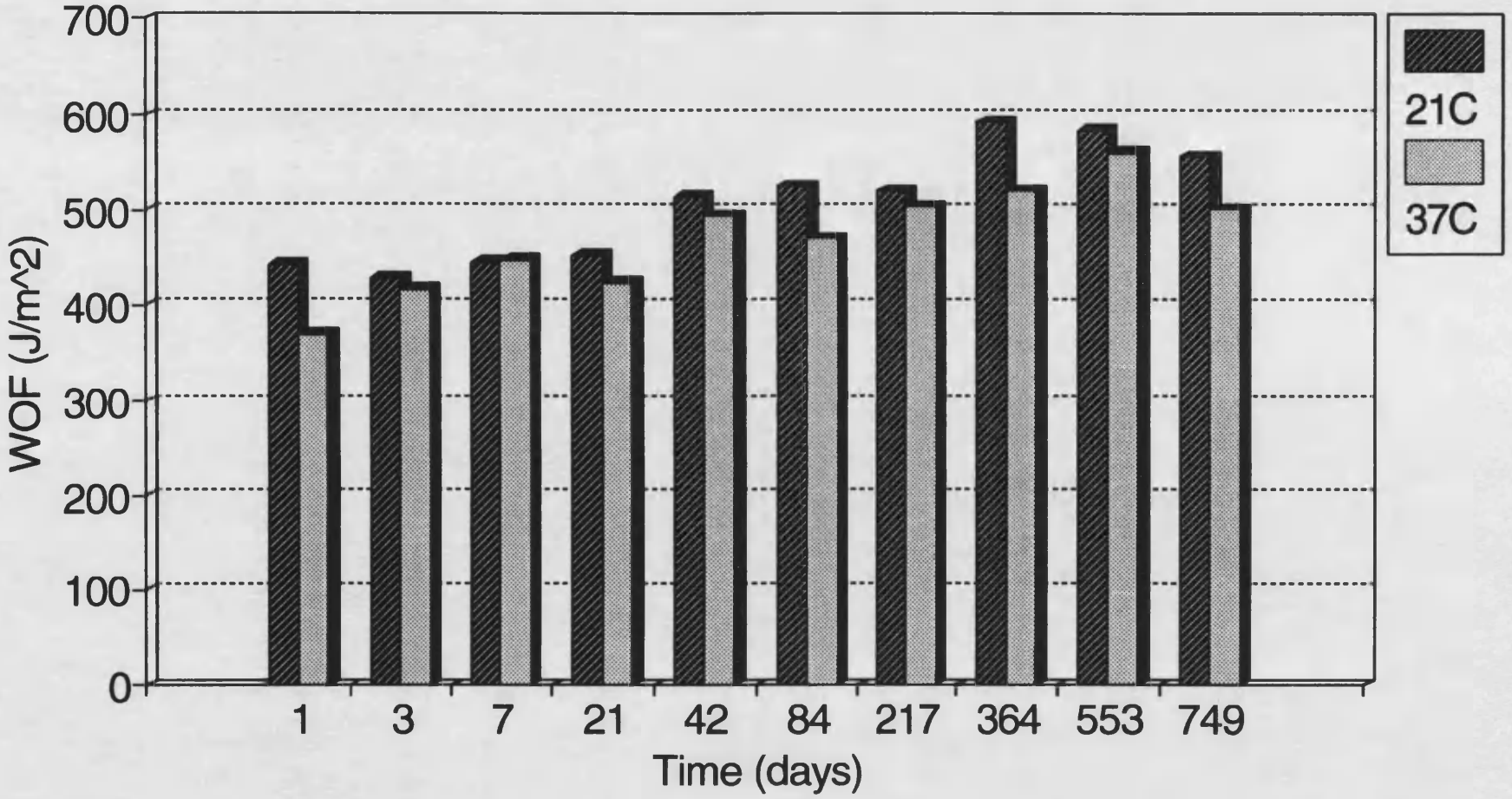


Figure 4.5 : WOF Results for
Normal Cement in Lipid

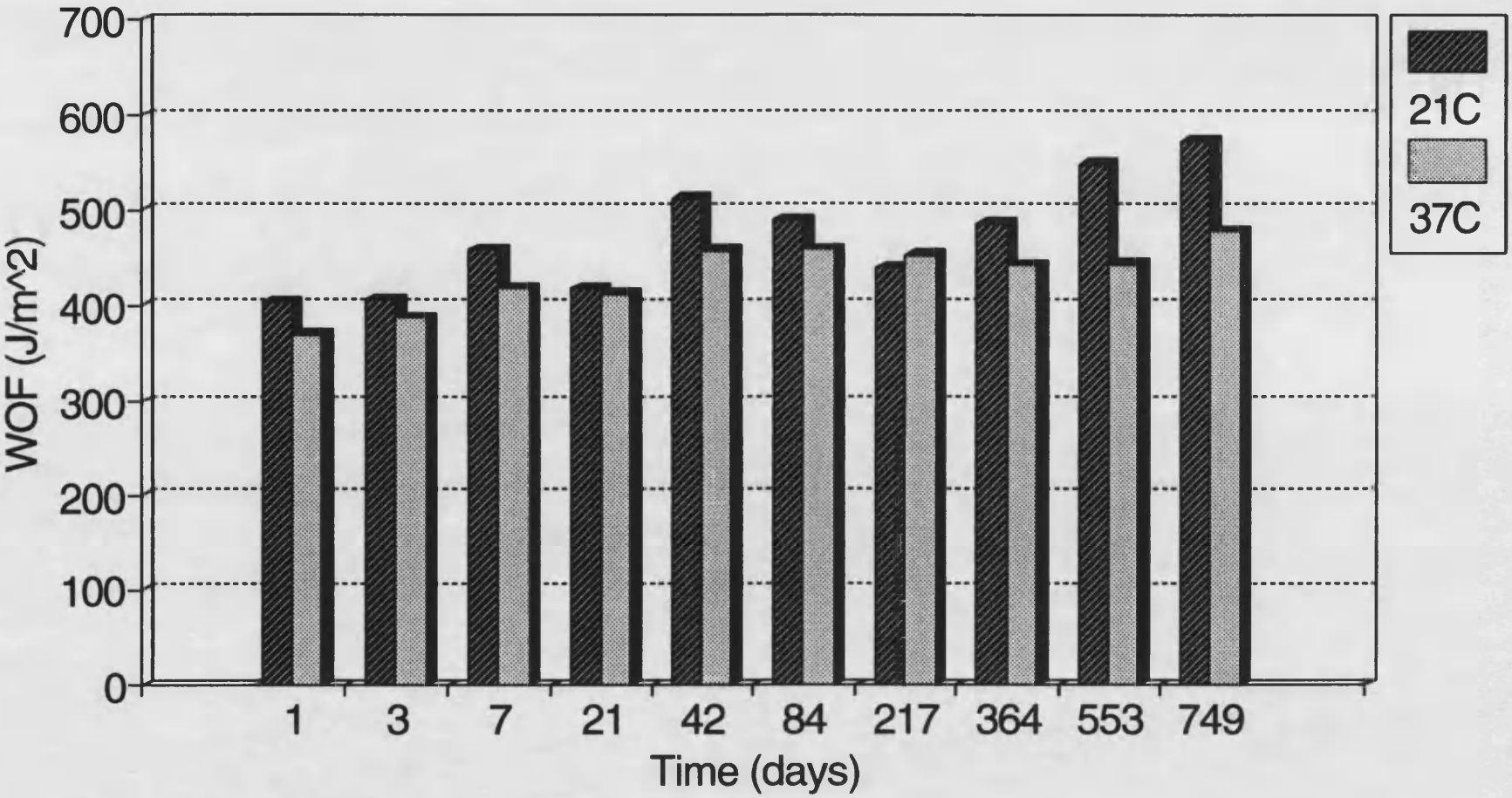


Figure 4.6 : WOF Results for
Normal Cement at 21C

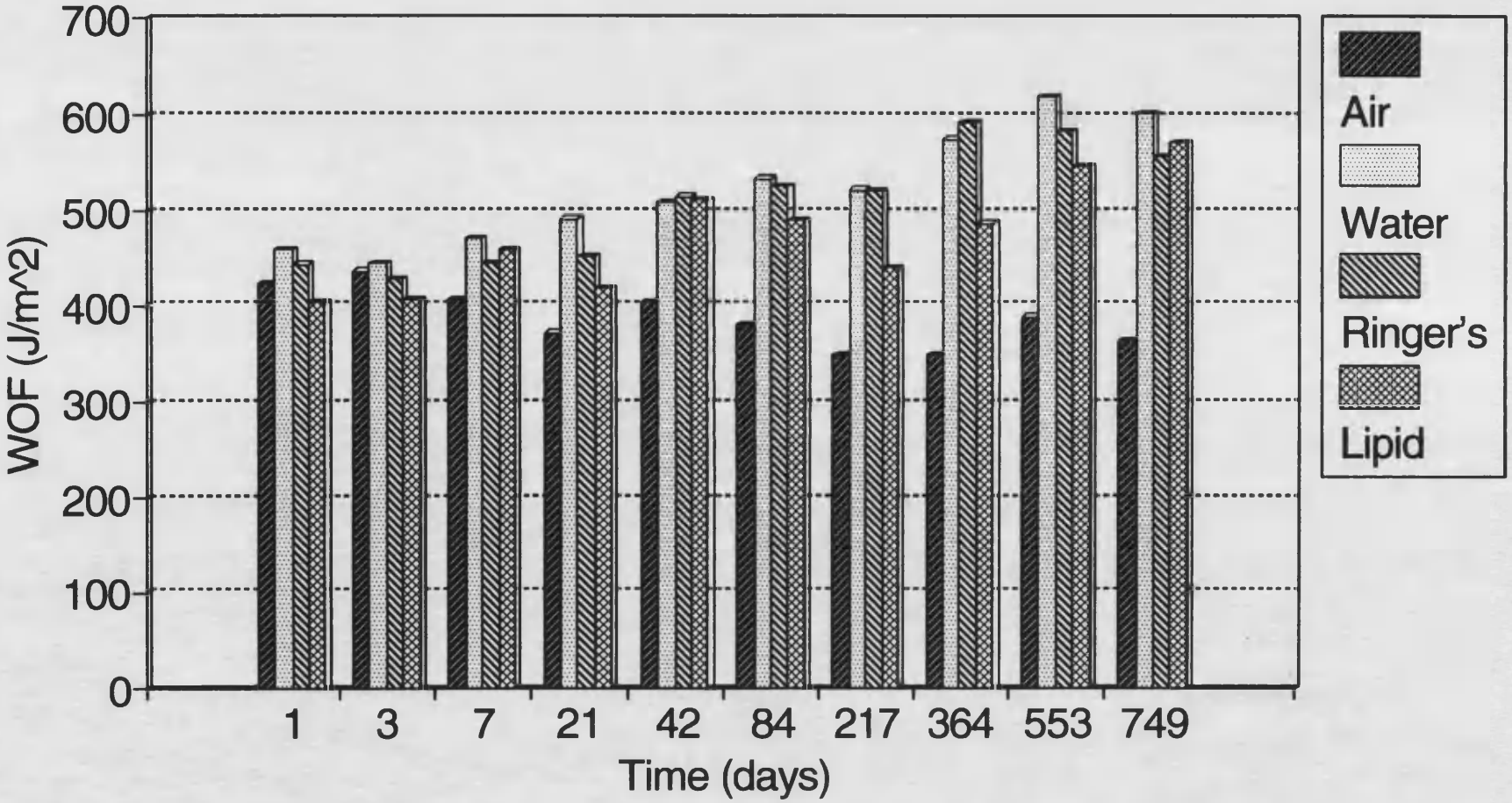


Figure 4.7 : WOF Results for
Normal Cement at 37C

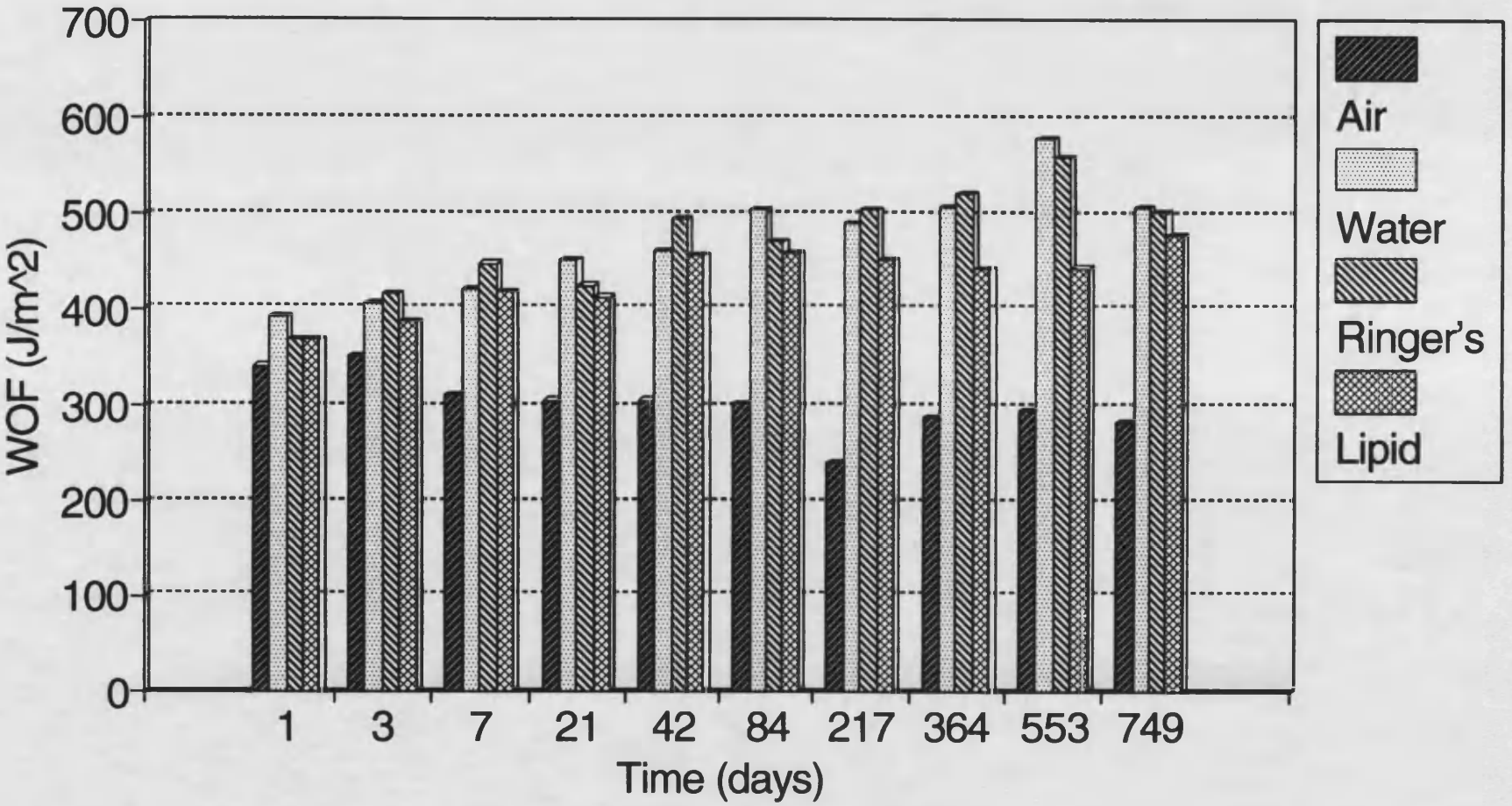


Figure 4.8 : WOF Results for
Normal Cement at 21C

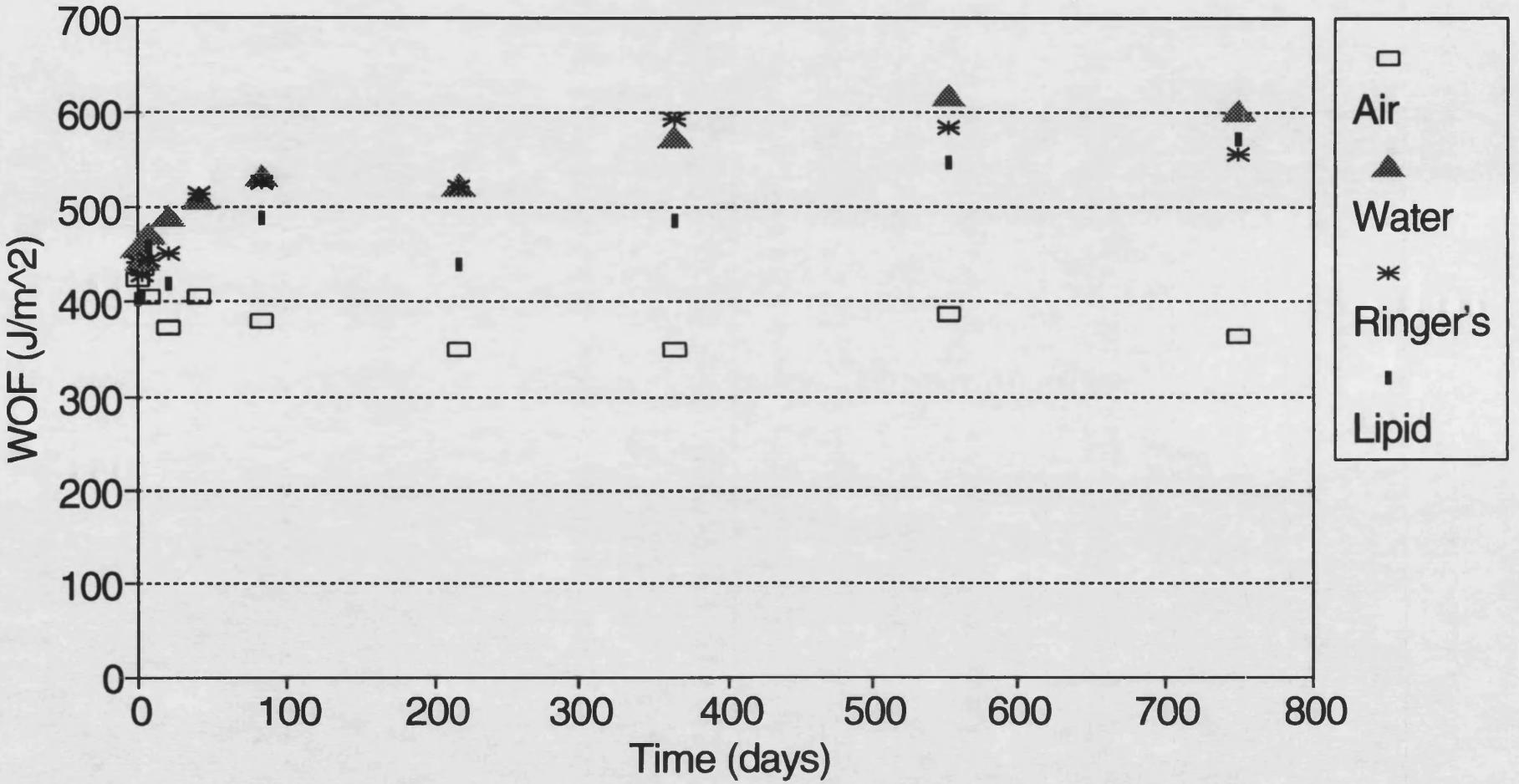


Figure 4.9 : WOF Results for
Normal Cement at 37C

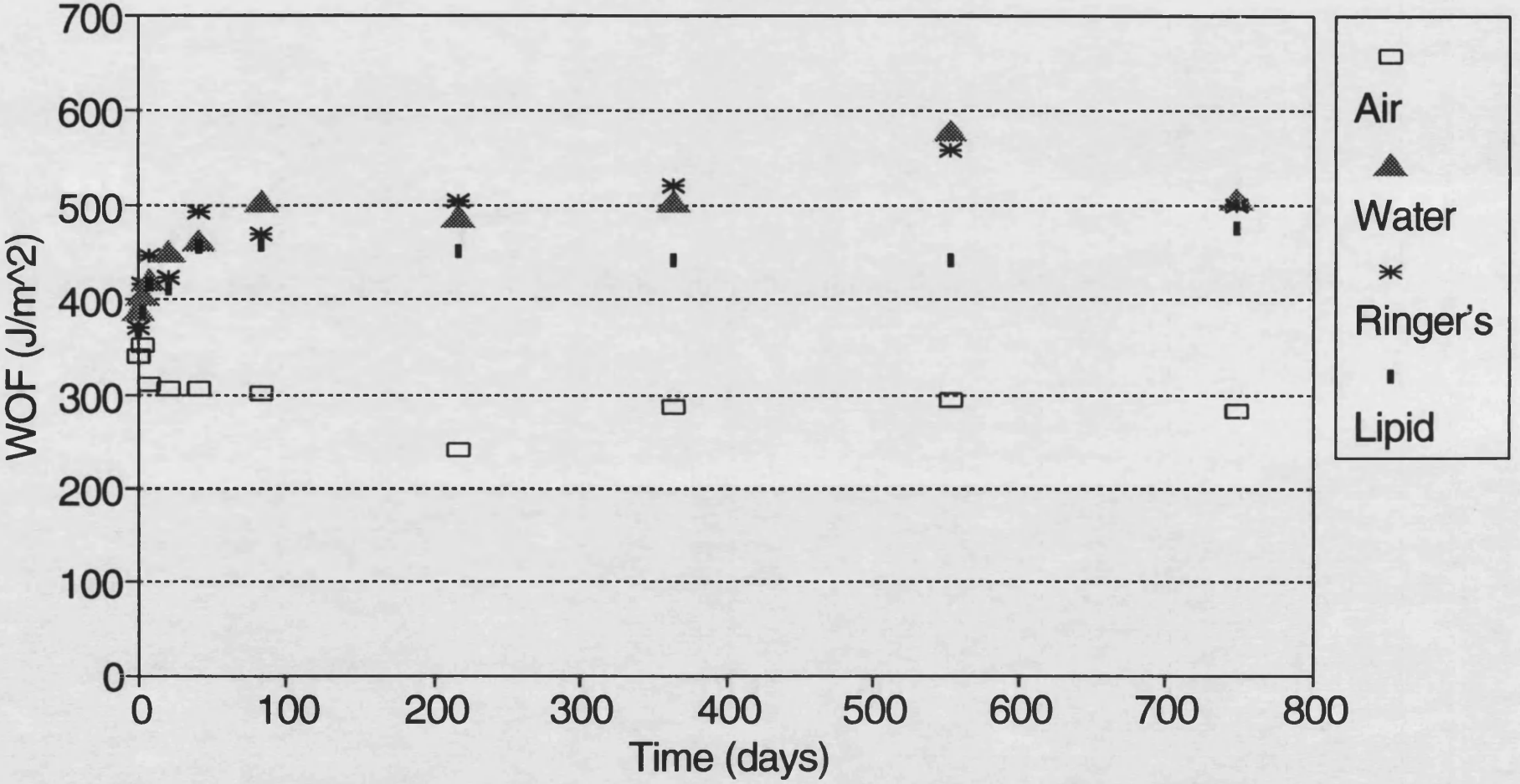


Figure 4.10 : WOF Results for
Fully Cured Cement in Air

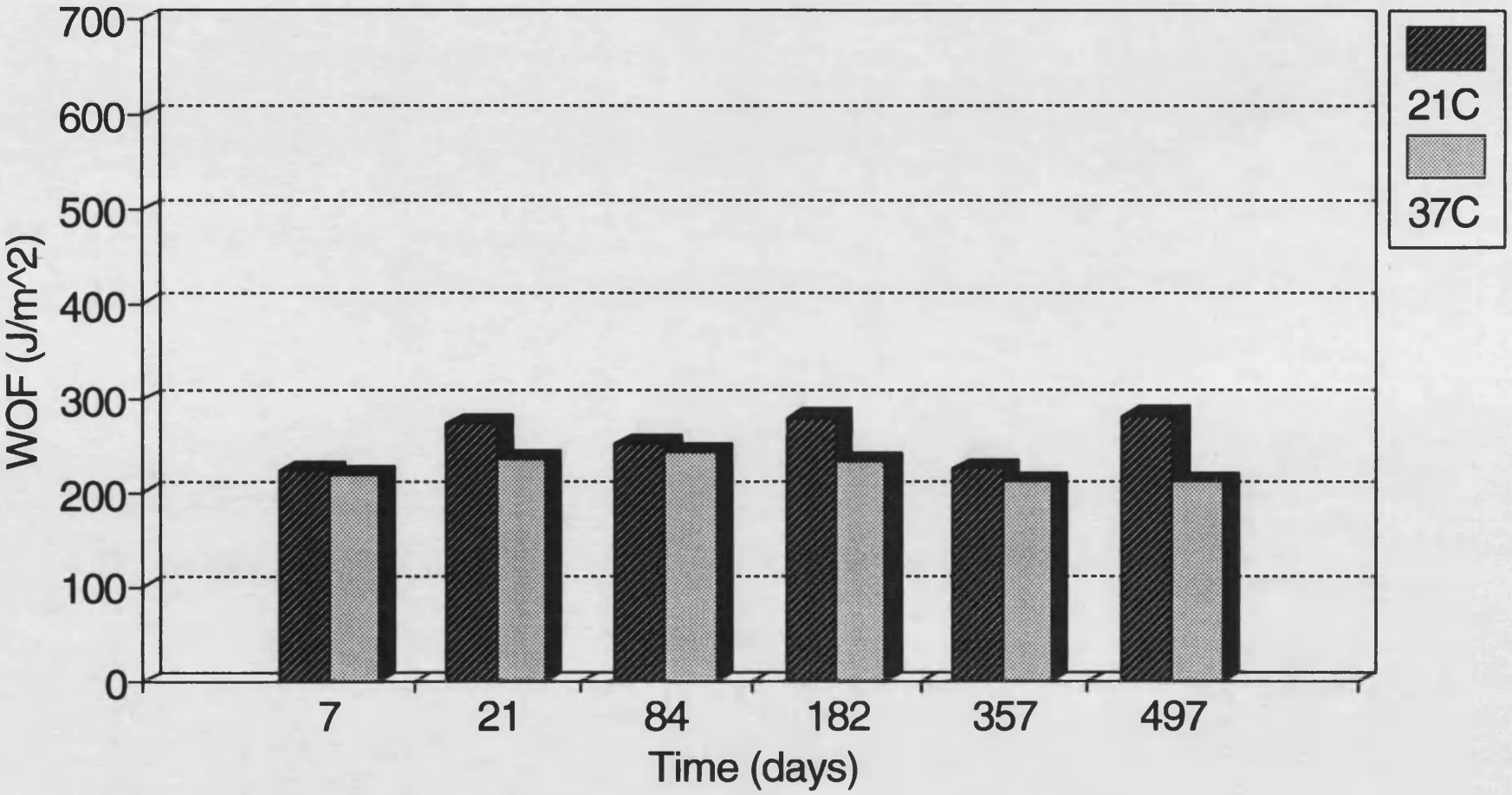


Figure 4.11 : WOF Results for
Fully Cured Cement in Water

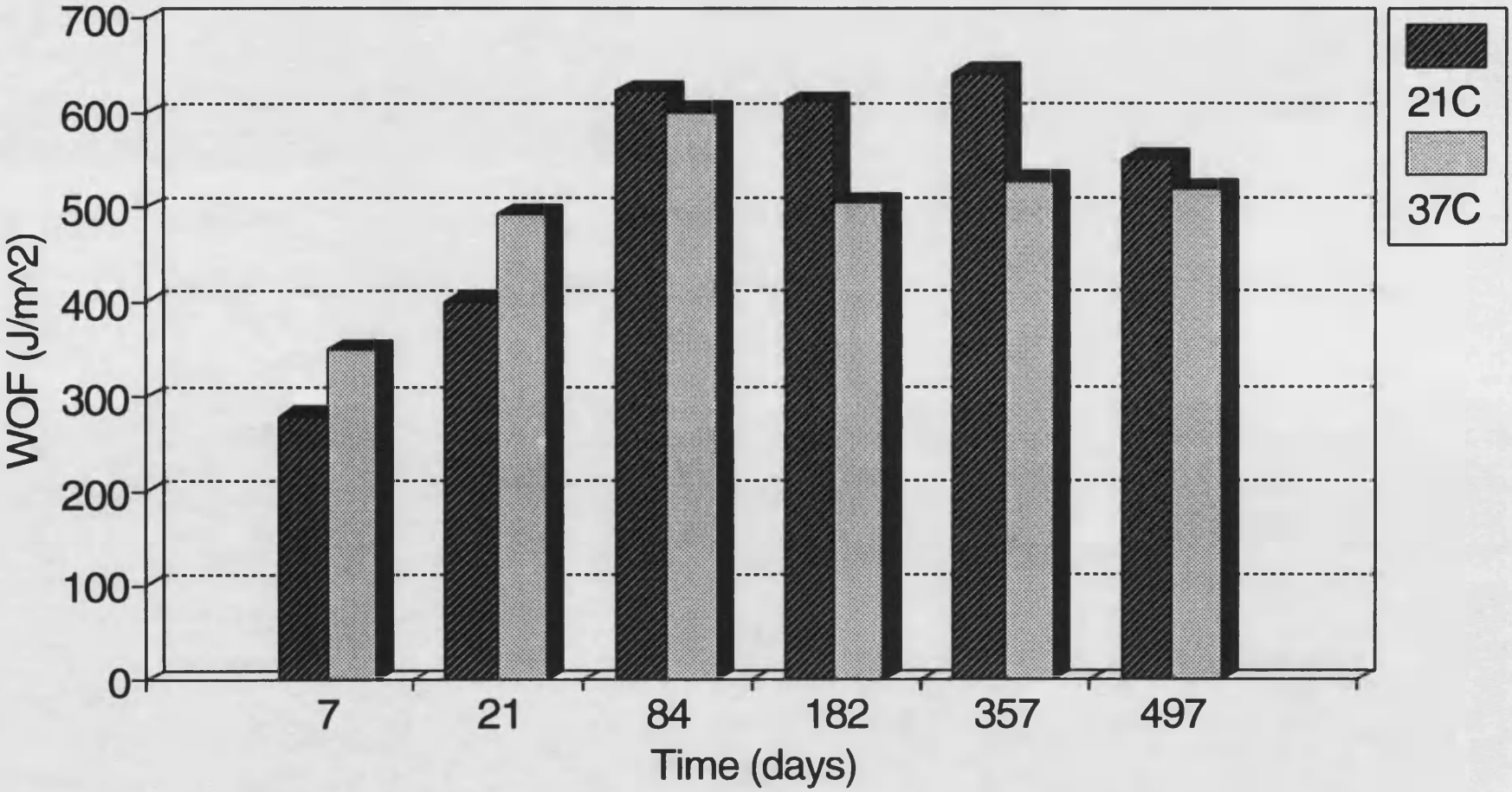


Figure 4.12 : WOF Results for
Fully Cured Cement in Ringer's

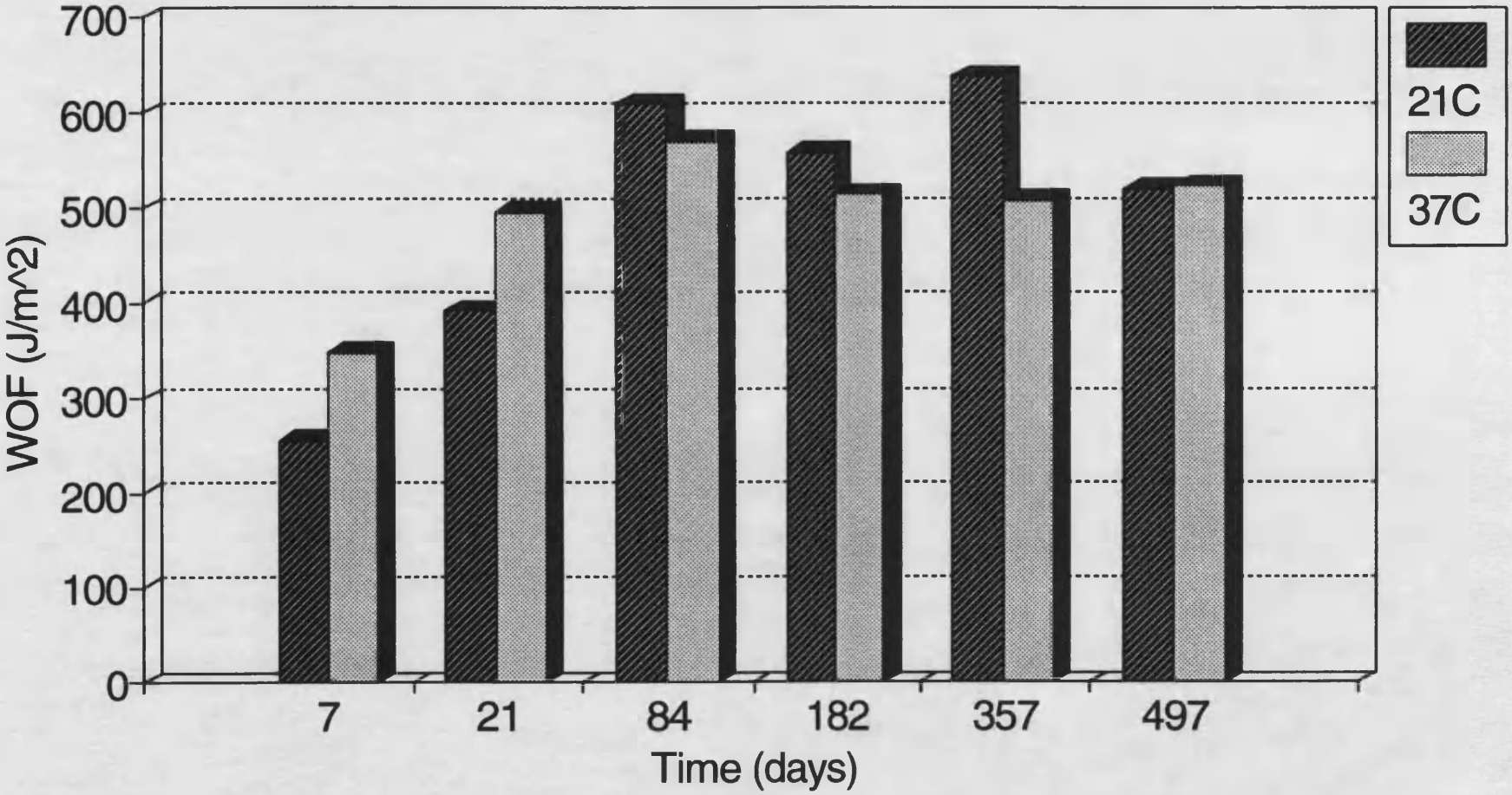


Figure 4.13 : WOF Results for
Fully Cured Cement in Lipid

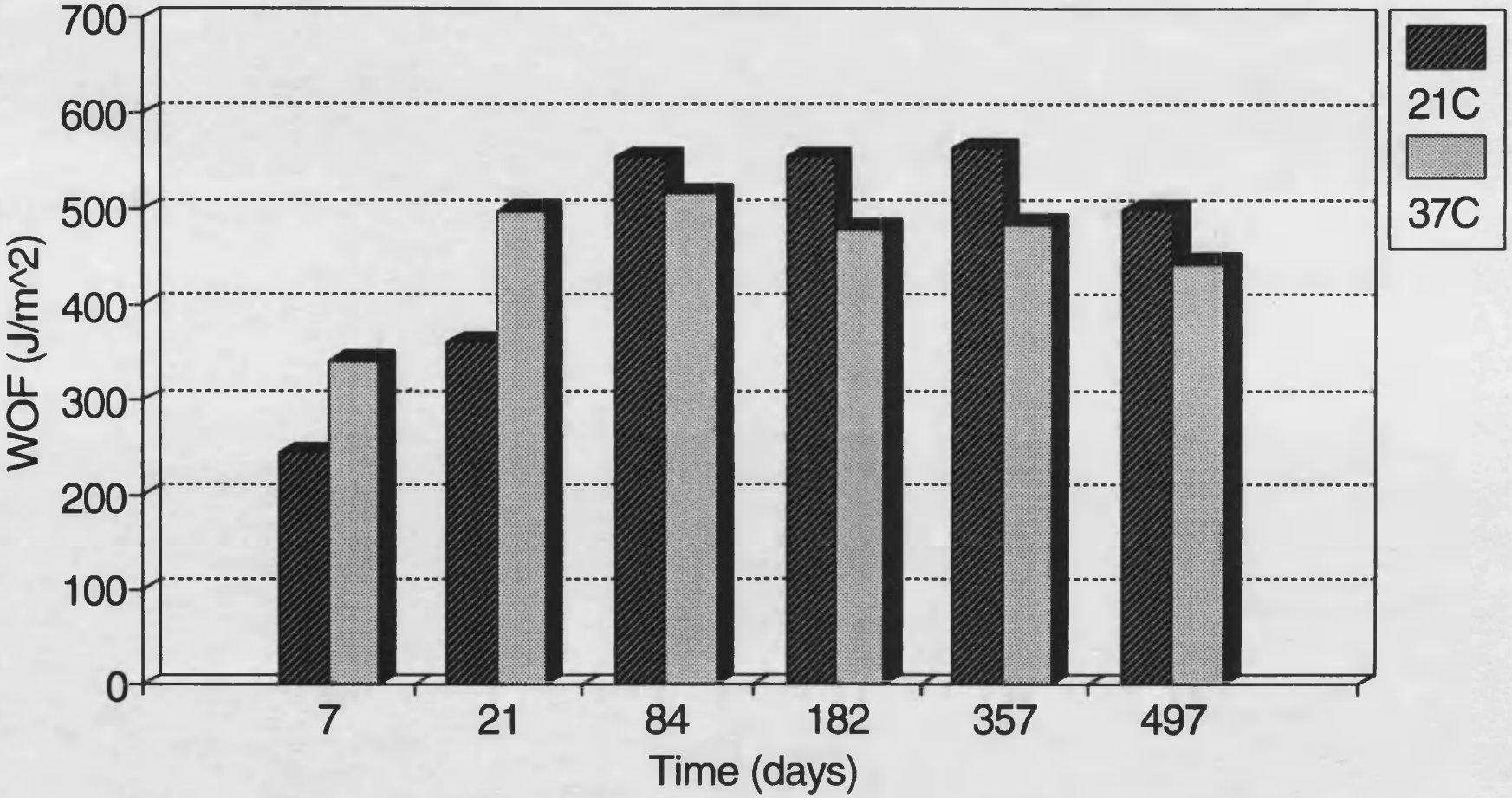


Figure 4.14 : WOF Results for
Fully Cured Cement at 21C

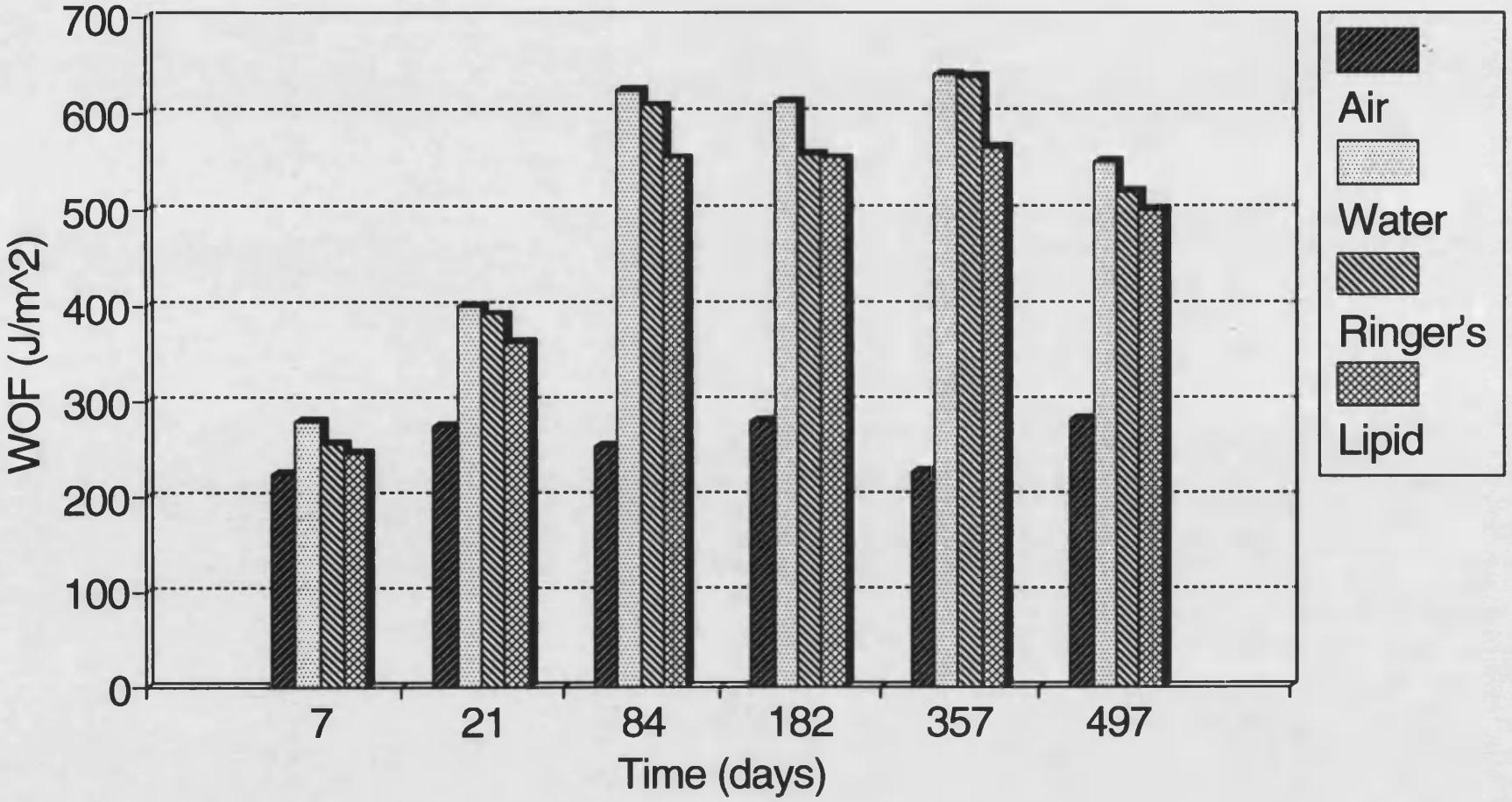


Figure 4.15 : WOF Results for
Fully Cured Cement at 37C

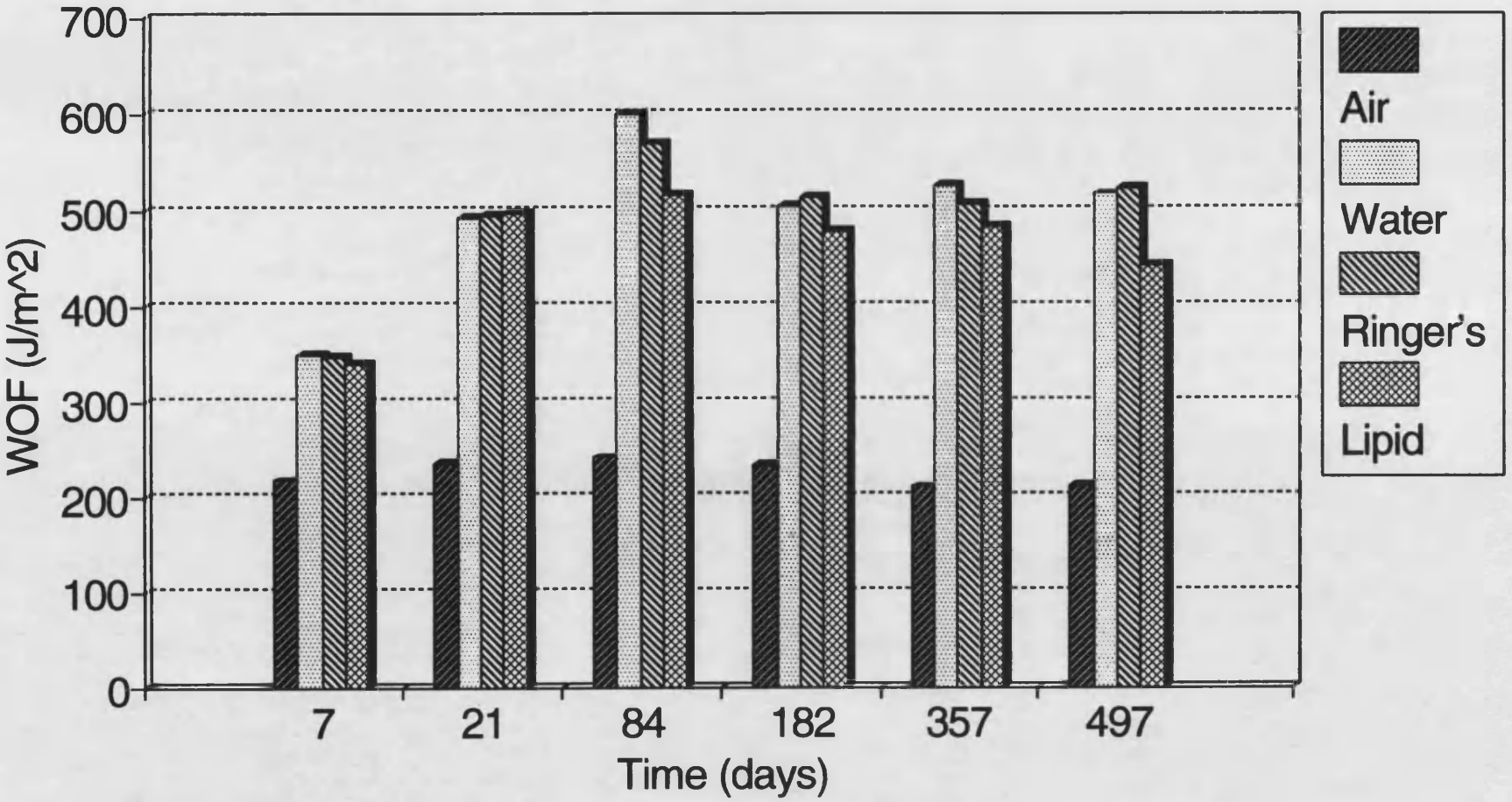


Figure 4.16 : WOF Results for
Fully Cured Cement at 21C

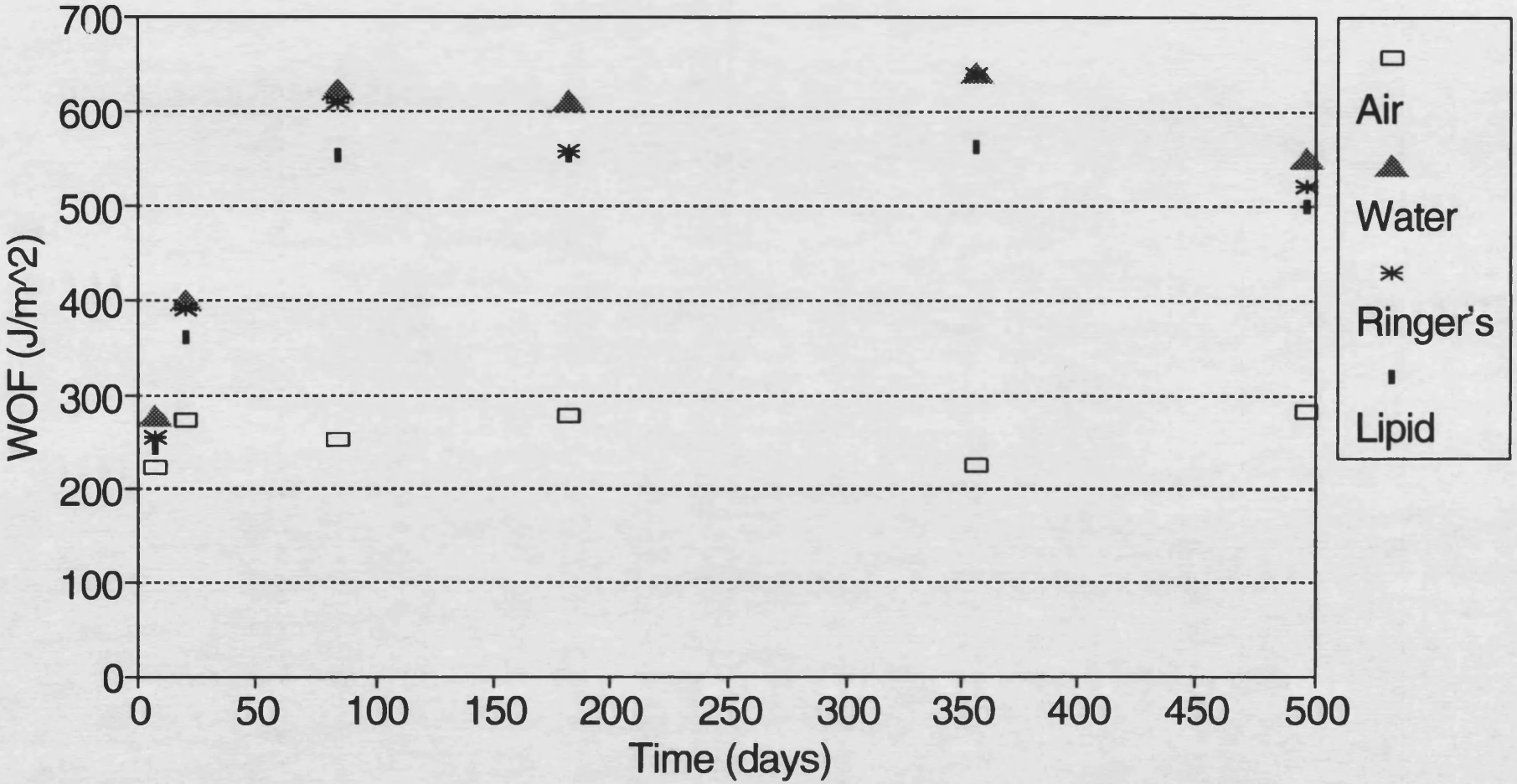


Figure 4.17 : WOF Results for
Fully Cured Cement at 37C

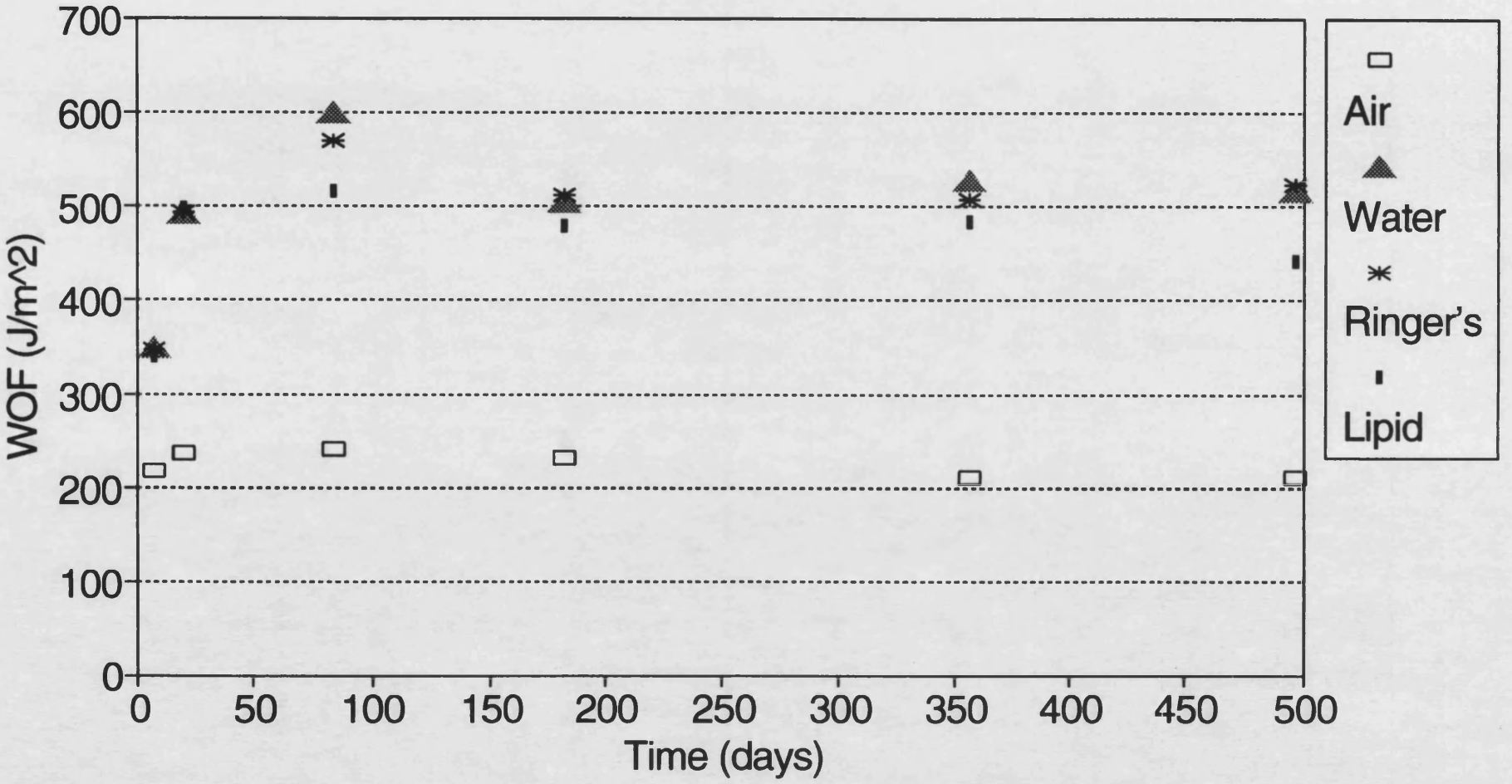


Figure 4.18 : Load-Displacement Curve
for a Typical Sample

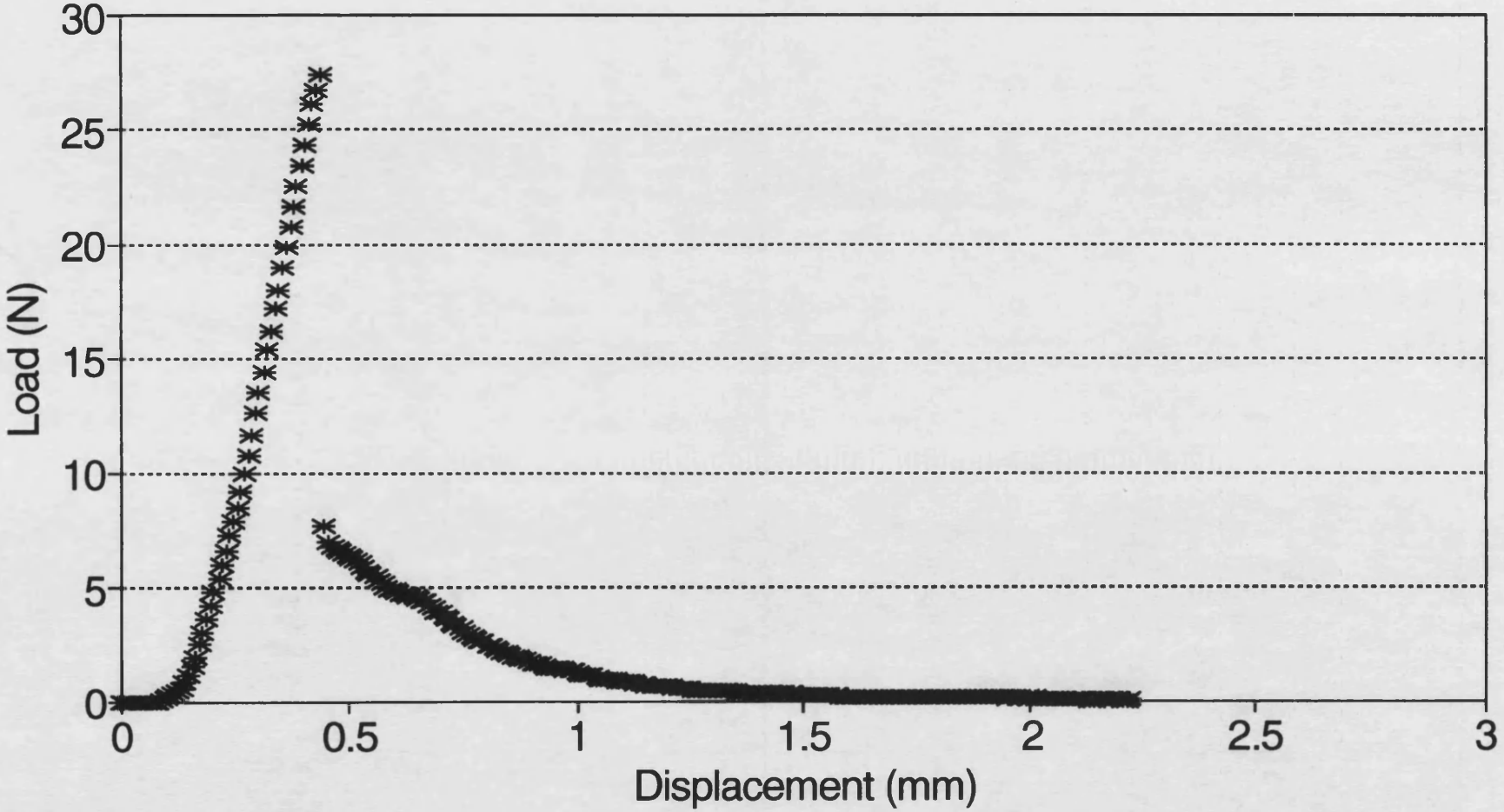


Figure 4.19 : Load-Displacement Curve
for a Sample Containing a Small Pore

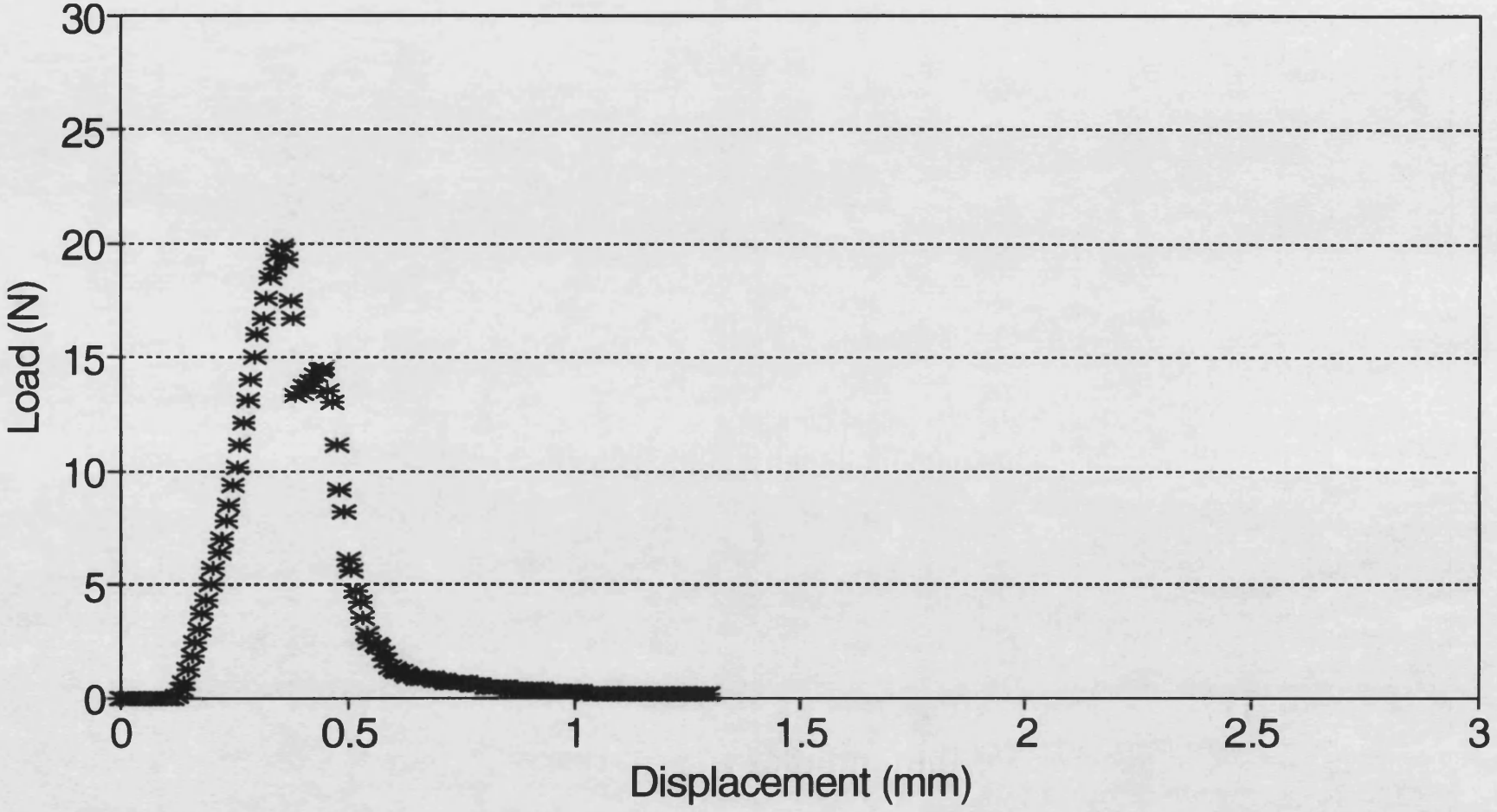


Figure 4.20 : Effect of Laboratory Temperature on the WOF of Cement

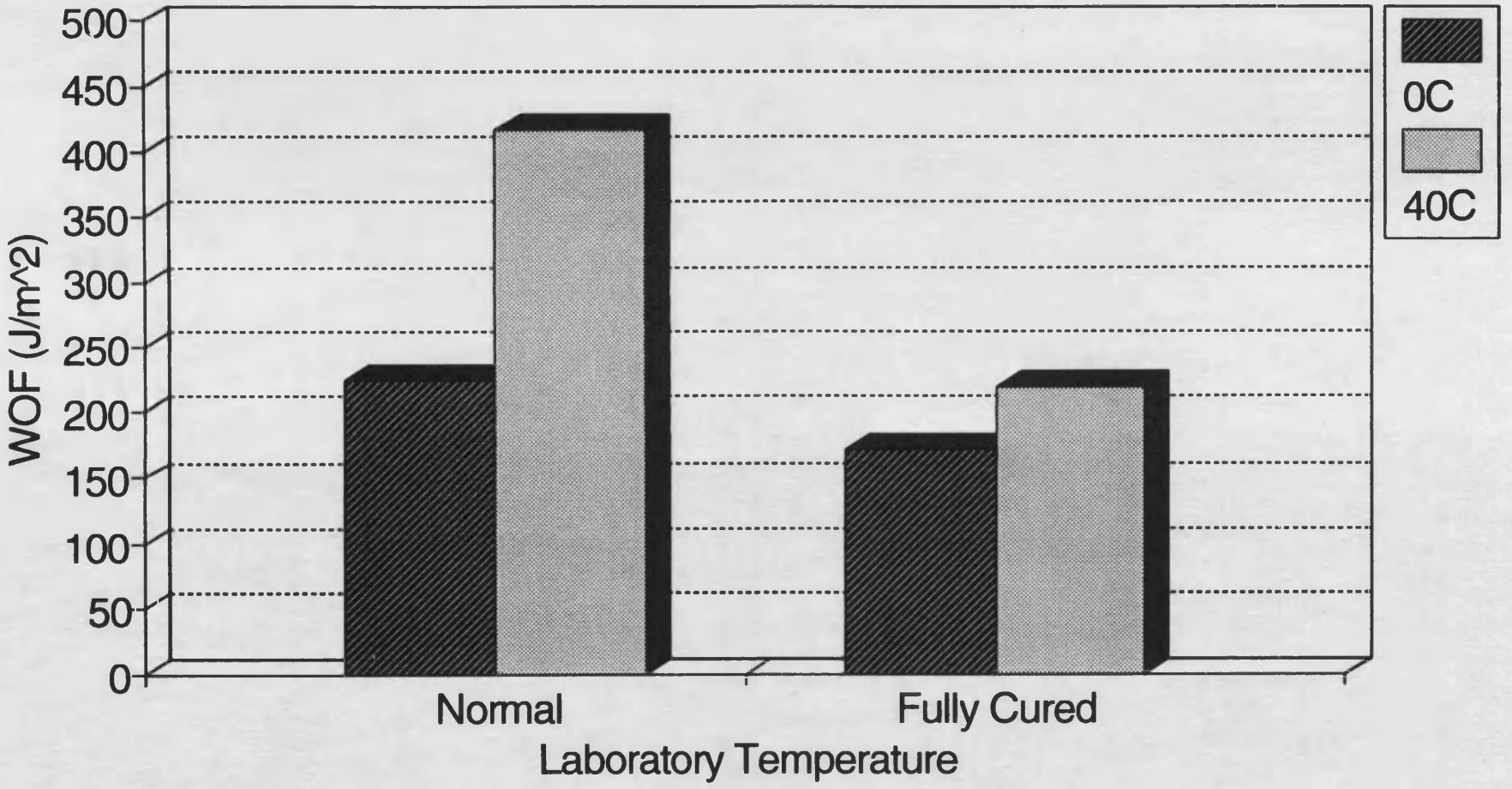


Figure 4.21 : Load-Displacement Curve
for Normal Cement Tested at 0C

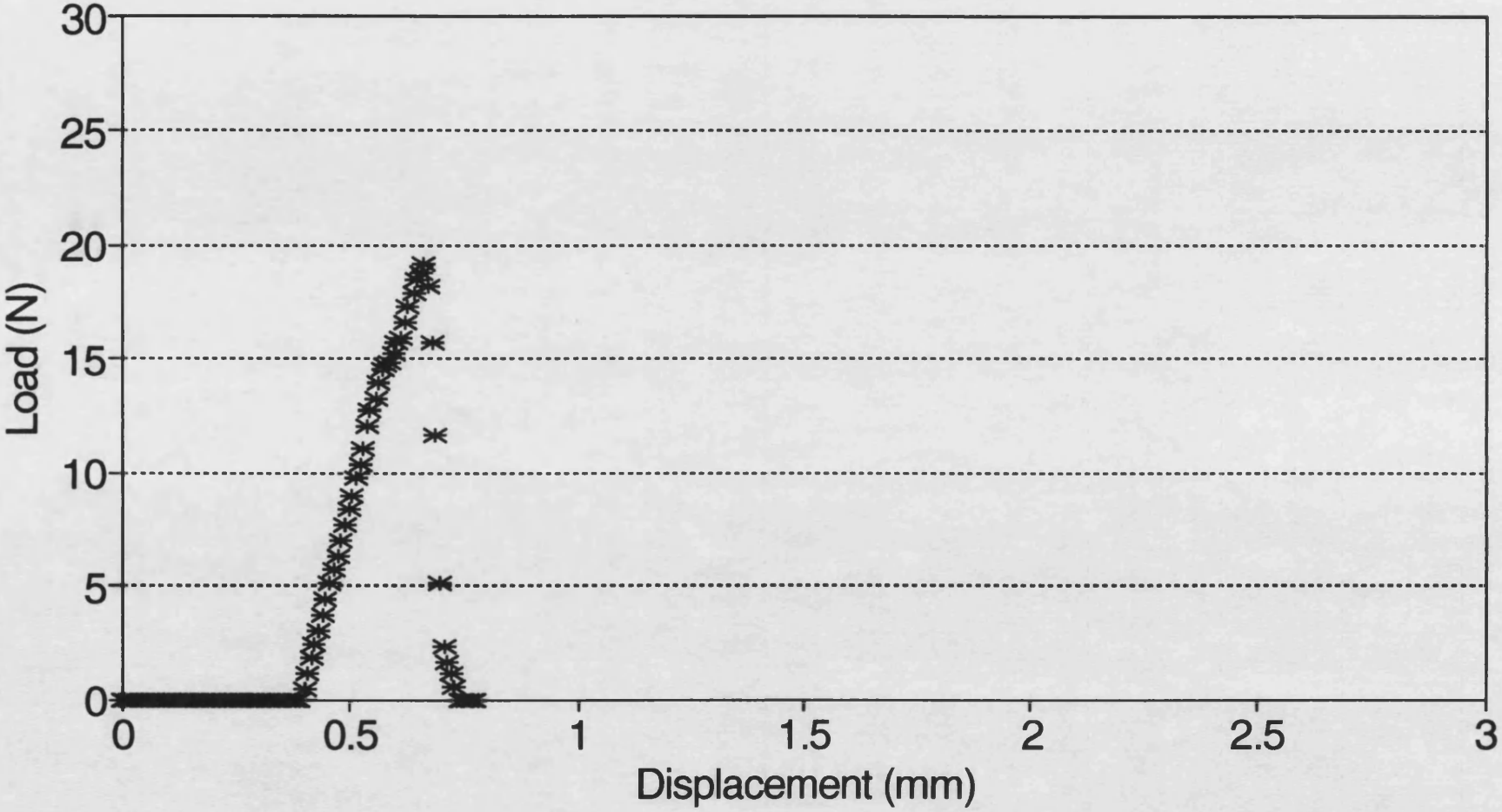


Figure 4.22 : Load-Displacement Curve
for Normal Cement Tested at 40C

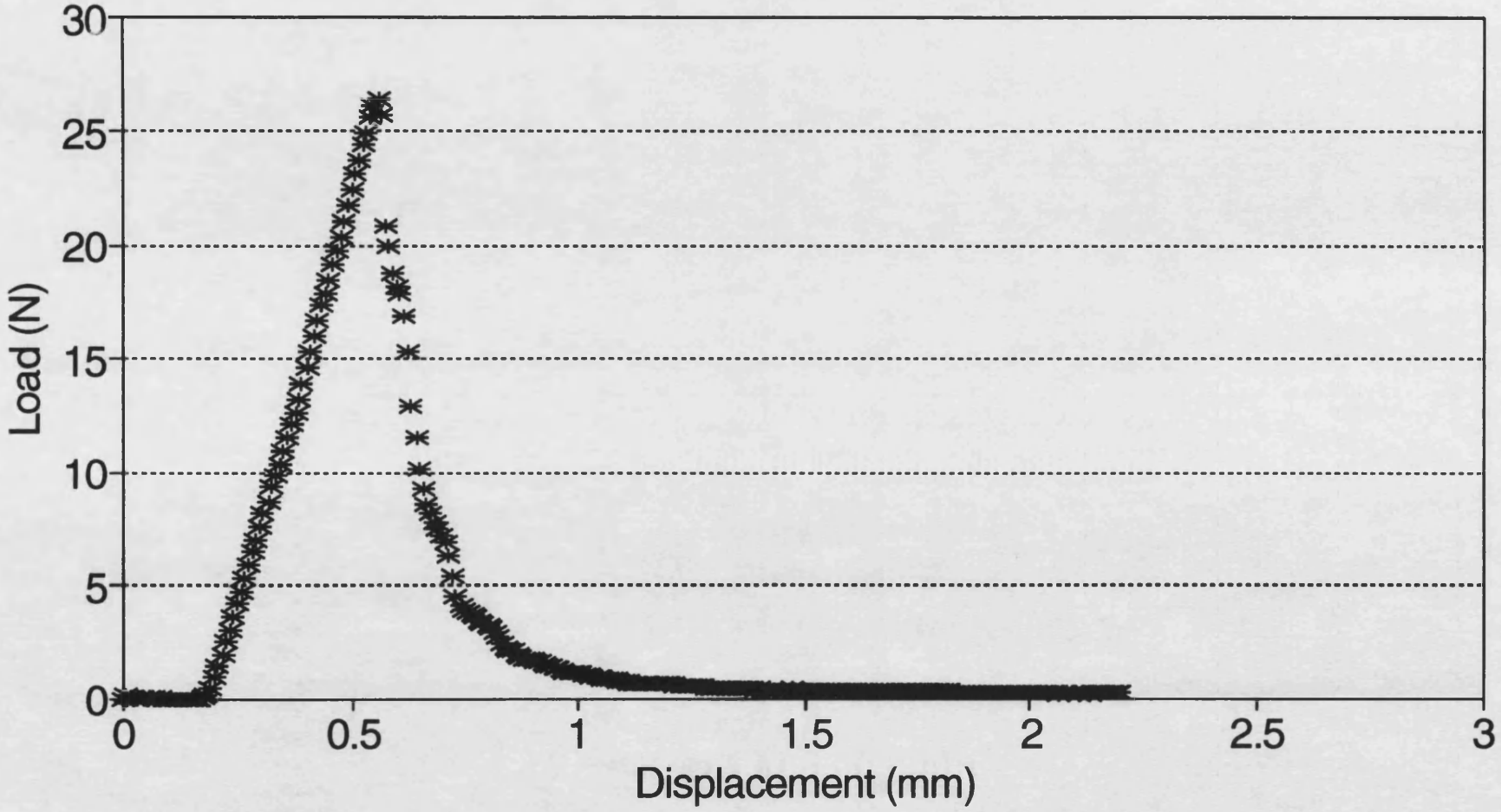


Figure 4.23 : Load-Displacement Curve
for Fully Cured Cement Tested at 0C

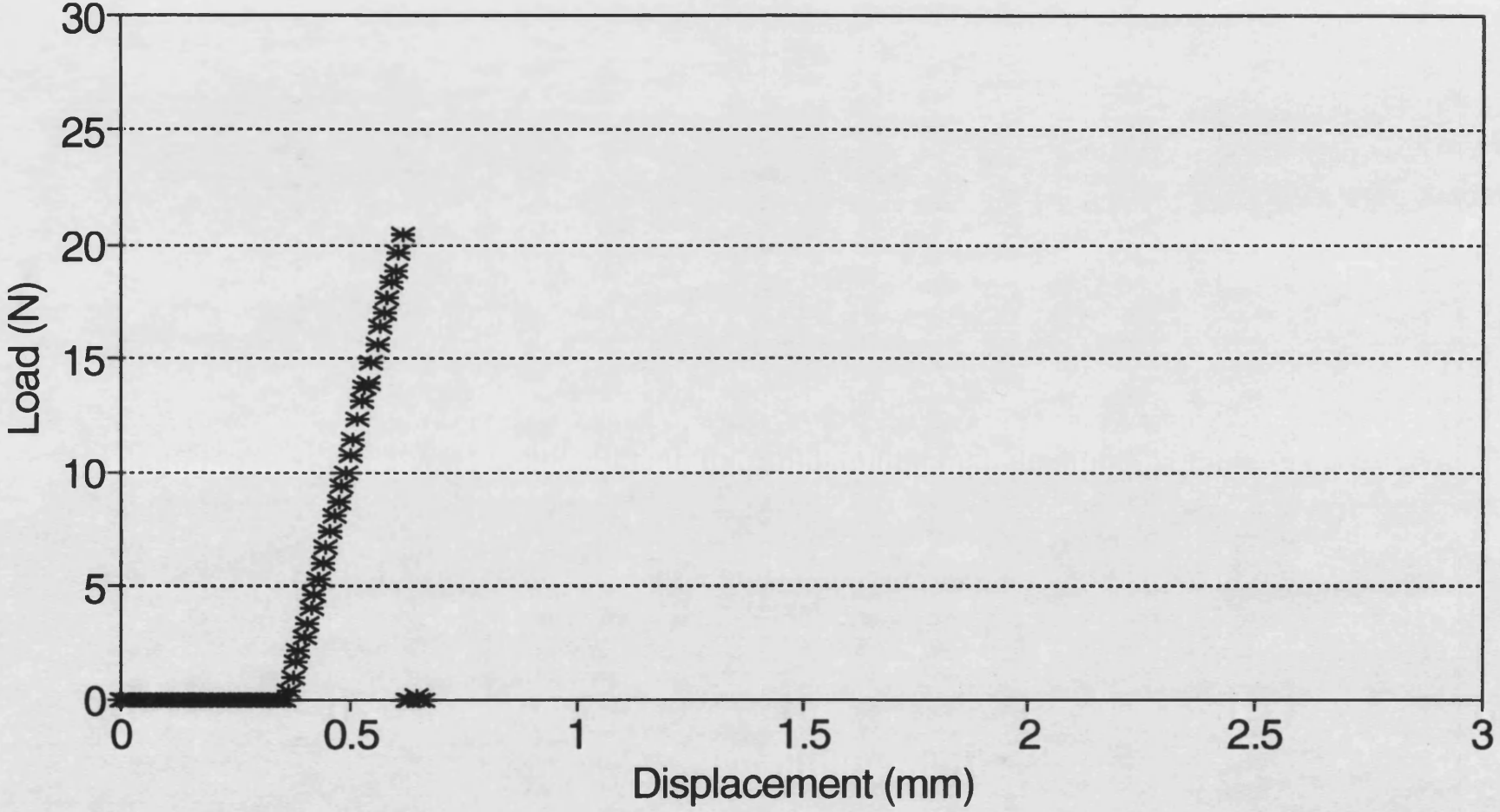


Figure 4.24 : Load-Displacement Curve
for Fully Cured Cement Tested at 40C

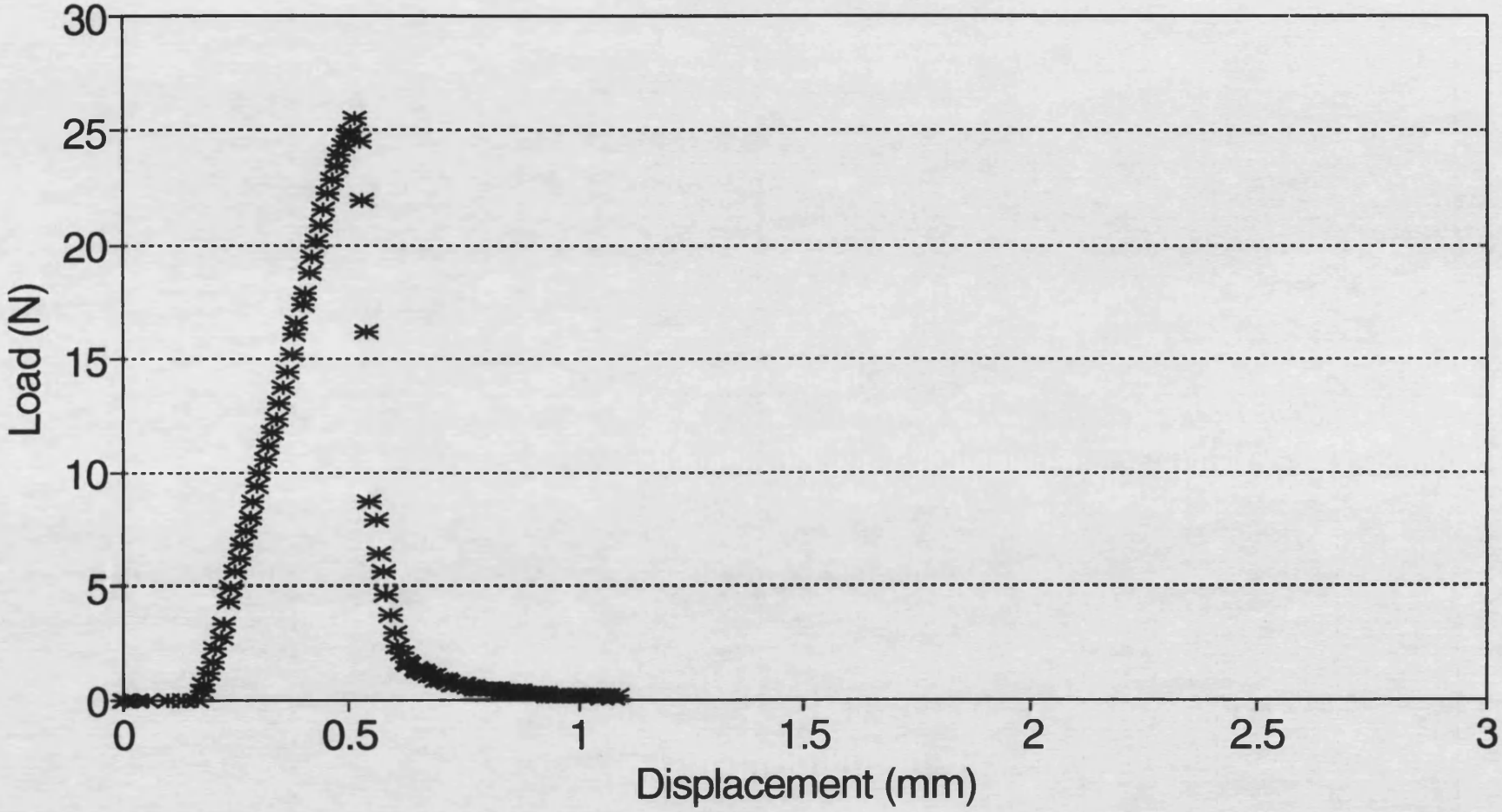
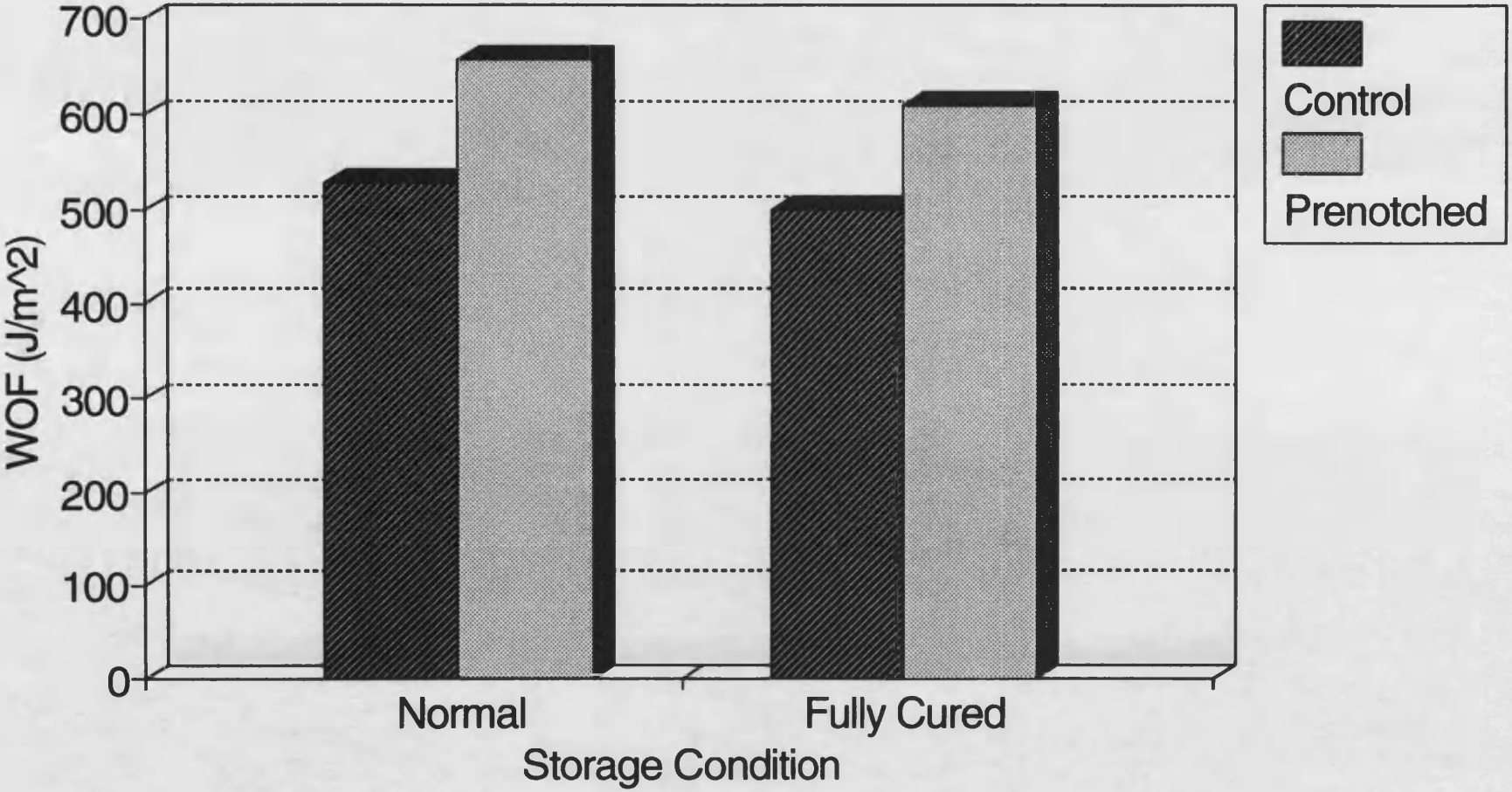


Figure 4.25 : Effect of Pre-notching on the WOF for Cement Stored in Water



5. RAPID FRACTURE

5.1 Rapid Fracture Results

5.1.1 Details of the Presentation of the Results

The rapid fracture tests measured the energy absorbed during impact fracture of the specimens of normal cement. This energy was then normalised to a WOF value to allow comparison with the results from the Tattersall-Tappin tests. Hence the results tables and graphs are presented in a similar manner to the Tattersall-Tappin (WOF) results. Again any samples containing gross (greater than 20%) porosity in the fracture surface were deemed to be unrepresentative and were thus disregarded.

The tables of results give the number of samples, mean WOF value, standard deviation, and 95% confidence interval (95%CI) for three different storage periods in each of the eight storage media.

The WOF results are also plotted graphically on sixteen separate graphs. These graphs all show time on the x-axis and have WOF plotted on the y-axis. To allow easier comparison of the results, the standard deviations are not shown on any of the graphs, but the statistical significance of the results are discussed in Appendix C.

The first four bar charts (Figures 5.1 - 5.4) show the rapid fracture results for samples stored in each of the four different media. Each bar chart corresponds to one the storage media and shows the rapid fracture results for samples stored at both 21°C and 37°C. Again the bars represent the mean WOF value at each of the storage periods studied. These bar charts allowed the general effects of storage in the different media on the WOF, as evaluated using this test method, to be identified. Presentation of the results in this format also allowed the results for the two storage temperatures to be compared.

The next two bar charts (Figures 5.5 and 5.6) show the rapid fracture results for each of the storage temperatures. Each bar chart corresponds to one of the storage temperatures, and shows the rapid fracture results for the four different media. The bars represent the average WOF for each of the storage media at the three time periods studied. Using these graphs the WOF results for the four different storage media could be compared.

The final two graphs (Figures 5.7 and 5.8) again show the rapid fracture results for the two storage temperatures, but are plotted as x-y graphs on a true time x-axis. The symbols represent the mean WOF values for the four storage media at each of the storage periods. From these graphs the effect of storage time in the various environments on the WOF could be ascertained.

There is a further set of eight bar charts which compare the WOF results for the two test methods (see Figures 5.9 - 5.16). Each bar chart compares the Tattersall-Tappin WOF results with those obtained from the rapid fracture tests, for samples stored for the same time period in each of the eight storage environments.

5.1.2 Results for Normal Cement

The WOF results evaluated from the rapid fracture tests are presented in Tables 5.1 - 5.8, with the mean WOF values shown graphically in Figures 5.1 - 5.8.

Figures 5.1 - 5.4 show the effect of storage time and temperature on the rapid fracture results for samples stored in air, water, Ringer's, and lipid respectively. From these bar charts it can be seen that there was no difference between the WOF for samples stored at 21°C and those at 37°C in any of the media. It can also be seen that there was no change in WOF with time for any of the storage environments.

Figures 5.5 and 5.6 show the rapid fracture results for samples stored at 21°C and 37°C respectively. The same results are also shown in Figures 5.7 and 5.8, where they are plotted on a true time x-axis. From these four figures it can be seen that there was no apparent difference between the WOF values for any of the four storage media. It can also be seen that, in all of the storage environments, the period of storage had no influence on the WOF.

The WOF results for the two different test methods are compared for each of the eight environments in Figures 5.9 - 5.16. Generally the WOF values obtained with the rapid fracture test method were found to be higher than those measured with the Tattersall-Tappin technique. This was due to the higher energy losses which were incurred with the rapid fracture test.

5.2 Discussion of Rapid Fracture

Section 5.1.2 showed that there was no correlation between WOF obtained from impact tests, and storage condition. The standard deviations with this test method were so large that any changes in the WOF with time or storage environment were completely masked. Hence none of the trends which were observed with the Tattersall-Tappin test could be identified with the rapid fracture test method.

It was also shown that the WOF obtained from rapid fracture tests was generally higher than that obtained from Tattersall-Tappin tests. This was due to greater energy losses with the rapid fracture test compared with the Tattersall-Tappin test. In the rapid fracture test energy was lost as the pendulum transferred energy to the specimens in the form of sound, and as kinetic energy which caused the specimens to be thrown from the test machine. The considerably greater energy losses associated

with the rapid fracture test led to the measurement of an artificially high value of the energy absorbed during fracture. In the Tattersall-Tappin test less energy was lost to the surroundings, thus giving a much more accurate measure of the WOF for the cement samples. These trends were also reflected in the much higher standard deviations for the rapid fracture test method compared with those from the Tattersall-Tappin test method.

5.3 Summary of Rapid Fracture Results

It was found that the storage conditions of the cement had no influence on the WOF as determined by rapid fracture tests. This was due to the greater energy losses and experimental variability with this test method compared to the Tattersall-Tappin test method. It was concluded that the Tattersall-Tappin test method provided a more accurate determination of the WOF of bone cement.

Table 5.1 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Air 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	13	738	88	738±53
21 days	14	728	128	728±74
84 days	16	675	87	675±46

Table 5.2 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Air 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	11	801	111	801±75
21 days	12	699	85	699±54
84 days	16	591	93	591±50

Table 5.3 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Water 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	12	795	90	795±57
21 days	13	765	78	765±47
84 days	16	758	90	758±50

Table 5.4 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Water 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	15	790	145	790±80
21 days	12	752	127	752±81
84 days	15	651	180	651±99

Table 5.5 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Ringer's 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	15	850	161	850±89
21 days	12	774	125	774±79
84 days	16	800	143	800±76

Table 5.6 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Ringer's 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	14	780	164	780±95
21 days	11	755	137	755±92
84 days	16	685	87	685±46

Table 5.7 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Lipid 21°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	16	827	108	827±58
21 days	13	713	89	713±54
84 days	16	872	166	872±88

Table 5.8 : Rapid Fracture Results for Normal Bone Cement Samples Stored in Lipid 37°C

Storage Time	No. of Samples	Mean Work of Fracture (J/m^2)	Standard Deviation	95% C.I.
7 days	15	805	95	805±52
21 days	14	769	91	769±53
84 days	14	707	67	707±39

Figure 5.1 : Rapid Fracture Results
for Normal Cement in Air

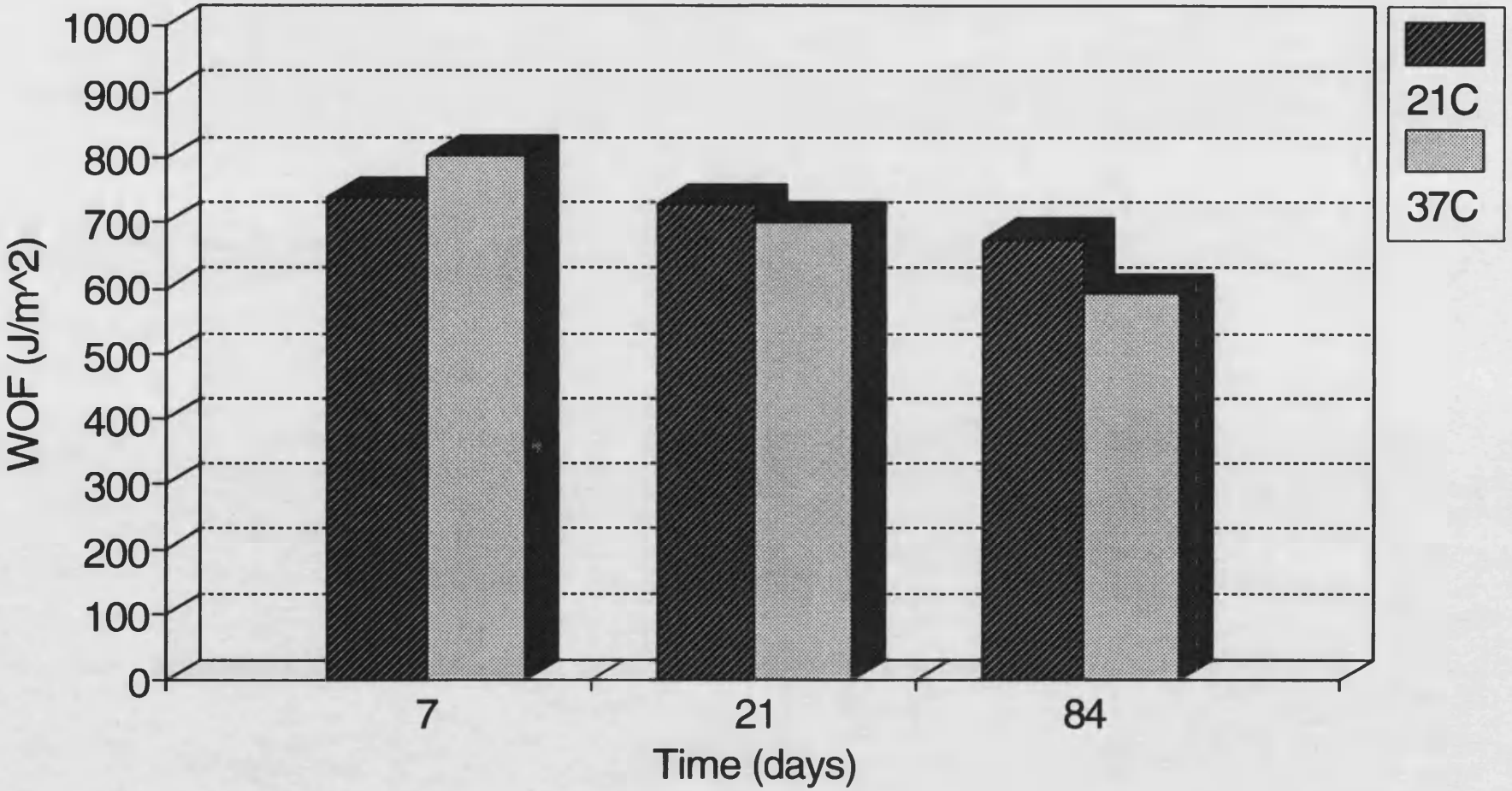


Figure 5.2 : Rapid Fracture Results
for Normal Cement in Water

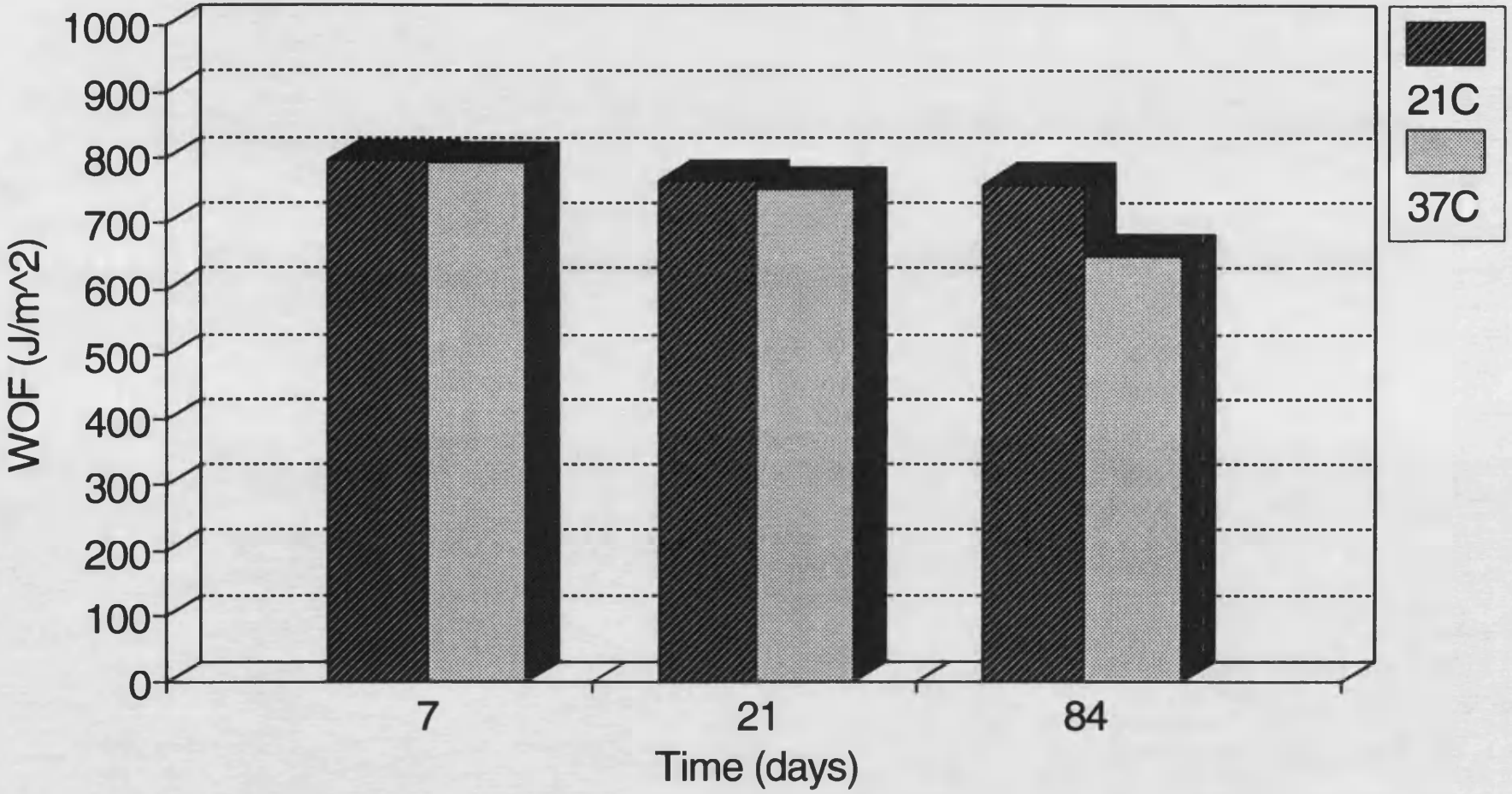


Figure 5.3 : Rapid Fracture Results
For Normal Cement in Ringer's

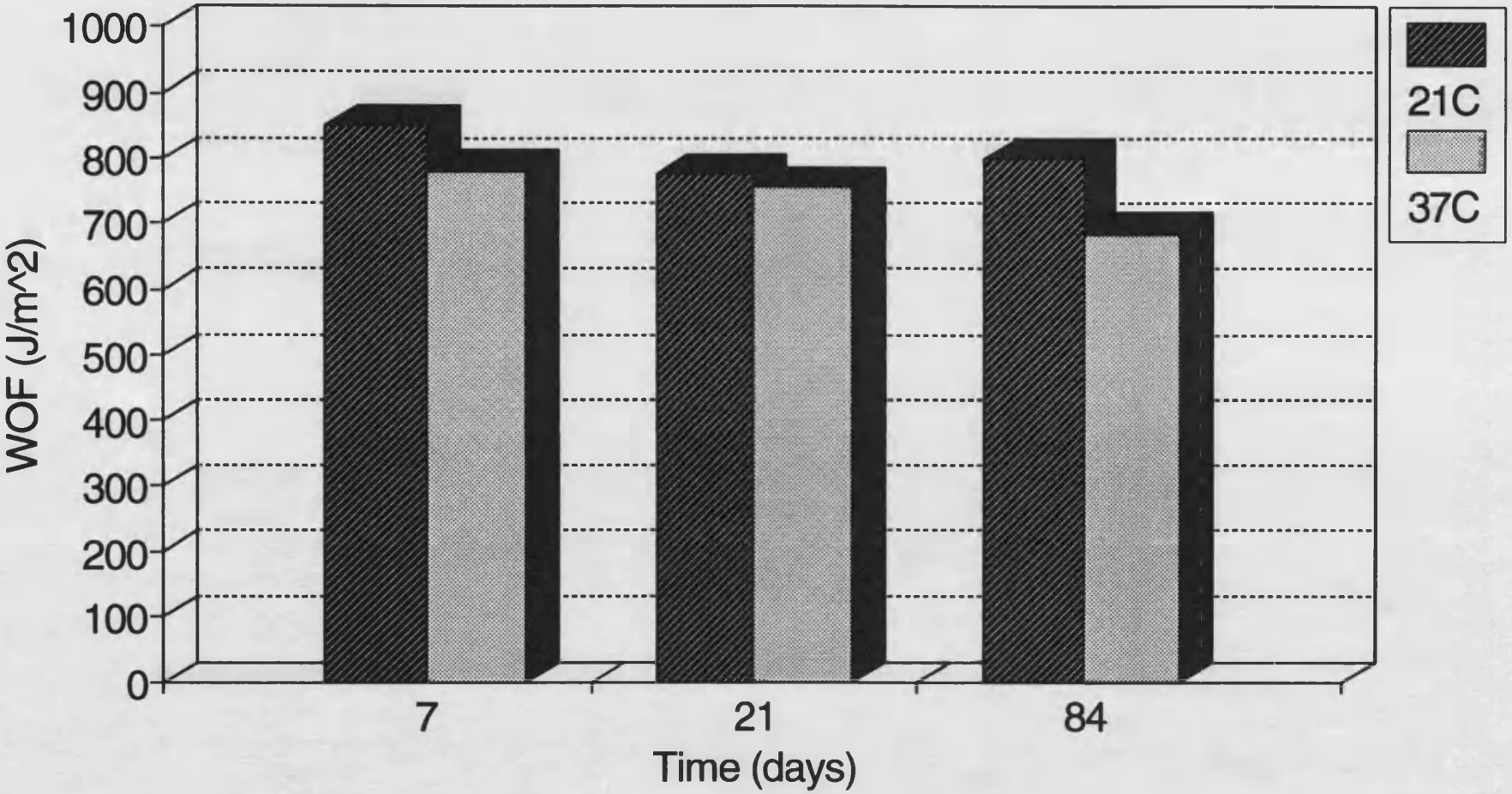


Figure 5.4 : Rapid Fracture Results
for Normal Cement in Lipid

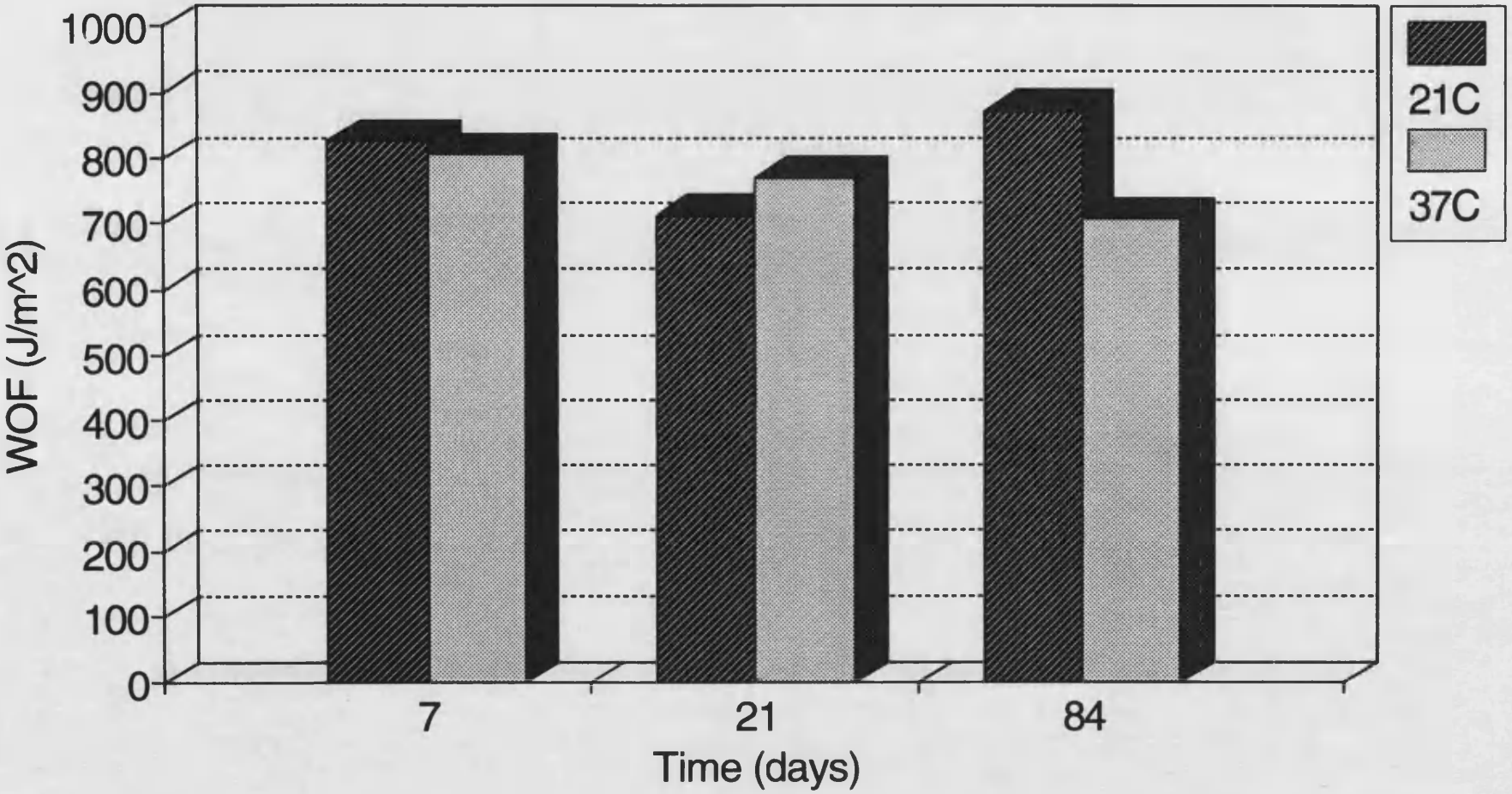


Figure 5.5 : Rapid Fracture Results
for Normal Cement at 21C

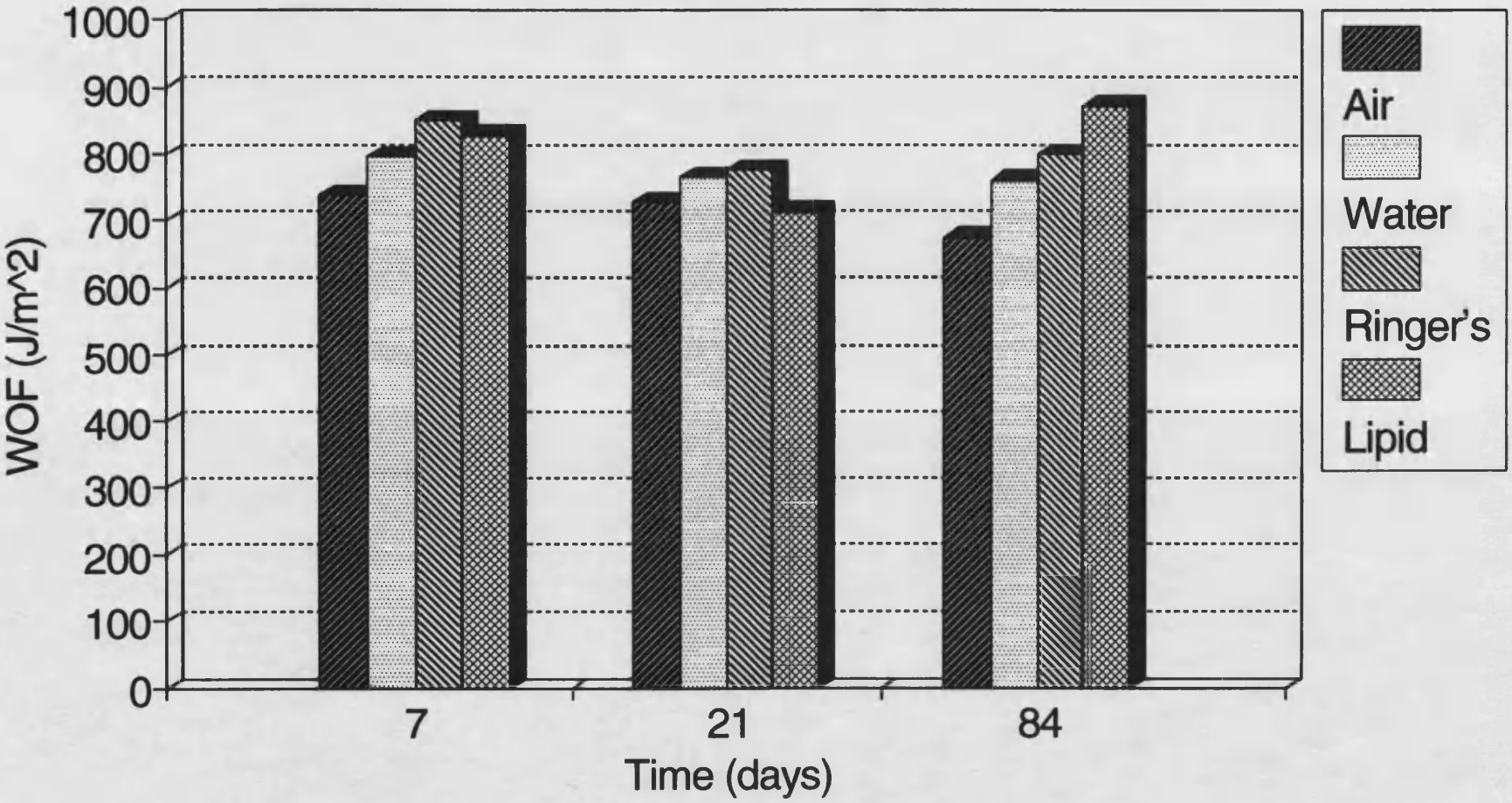


Figure 5.6 : Rapid Fracture Results
for Normal Cement at 37C

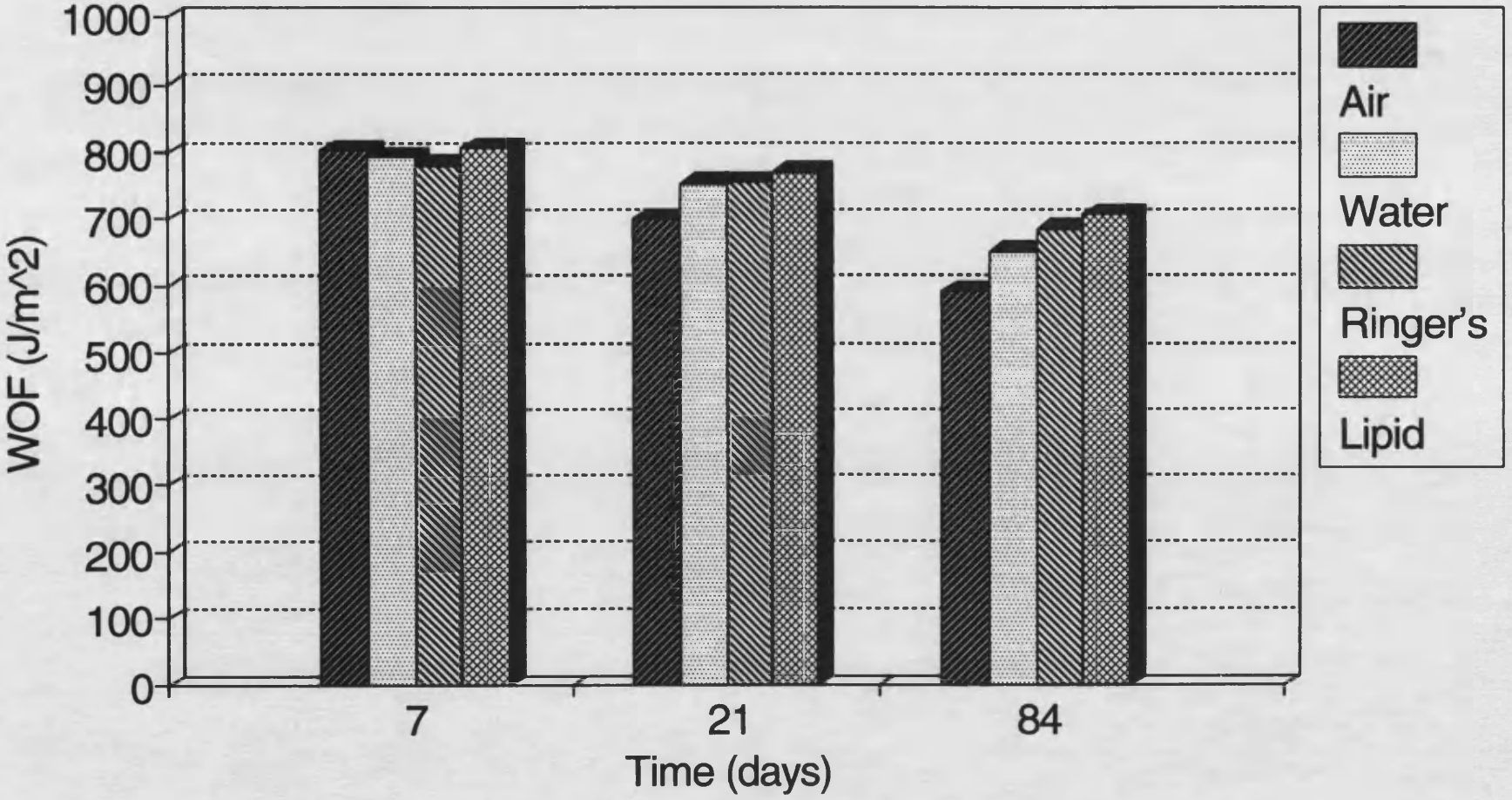


Figure 5.7 : Rapid Fracture Results
for Normal Cement at 21C

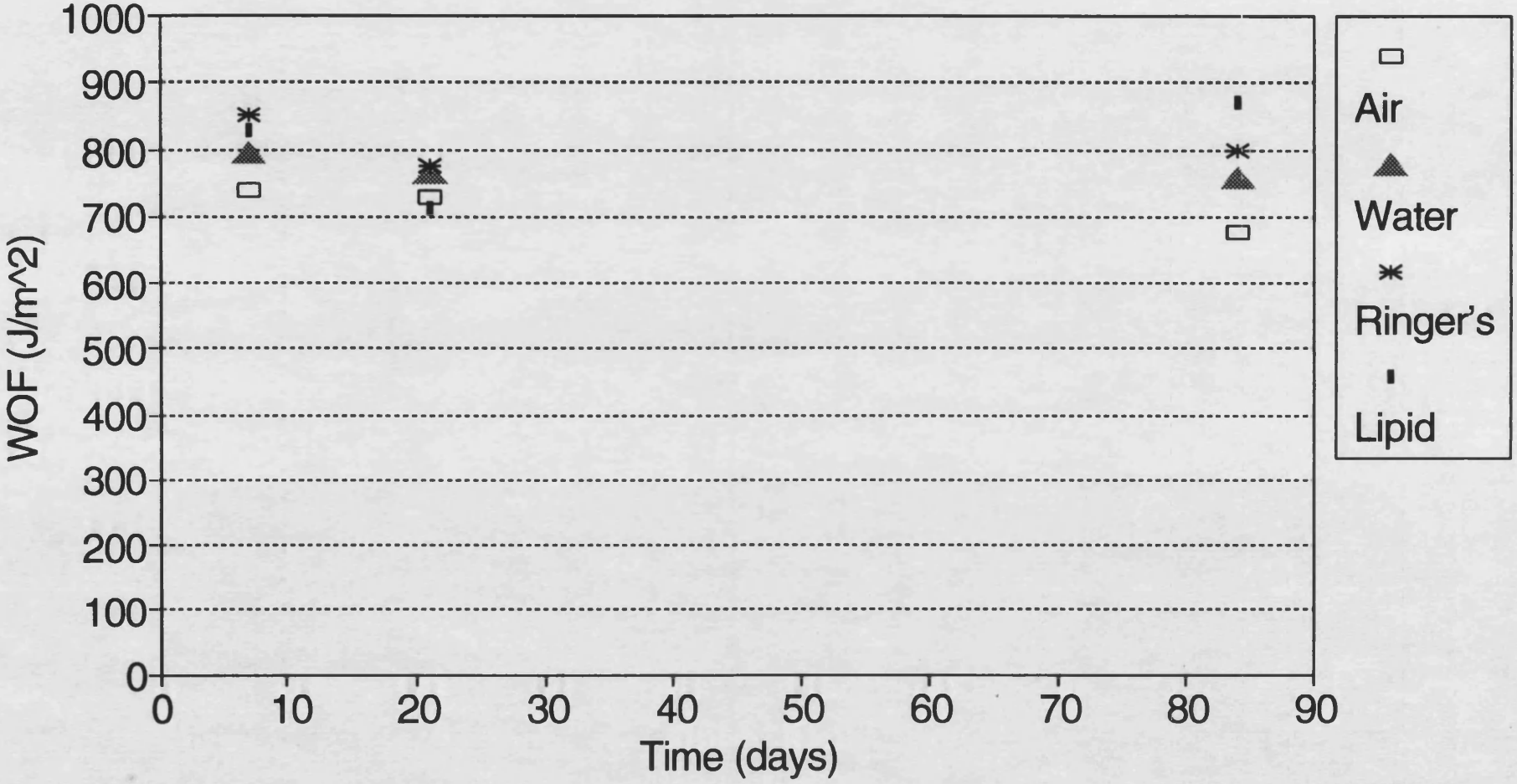


Figure 5.8 : Rapid Fracture Results
for Normal Cement at 37C

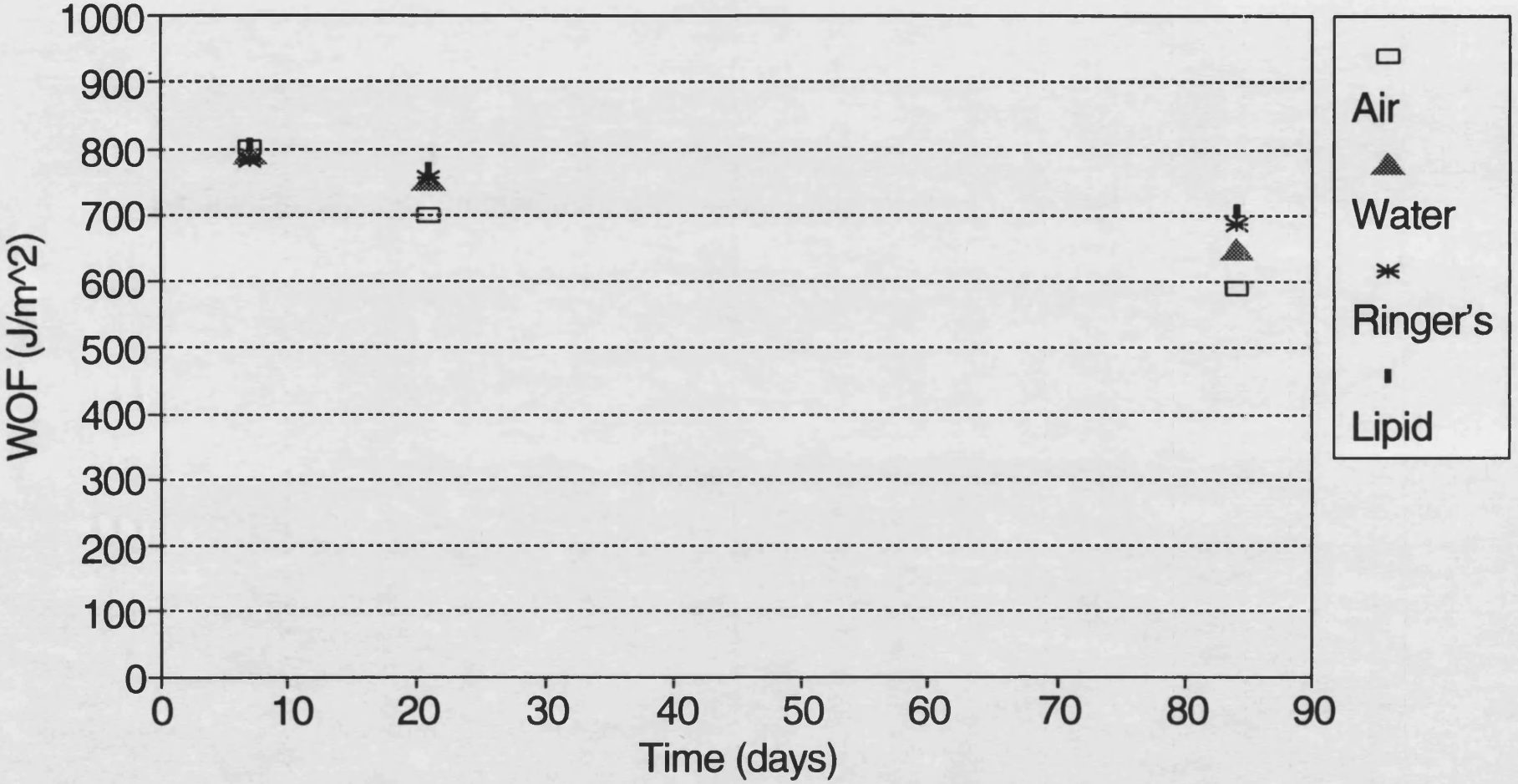


Figure 5.9 : WOF Results versus Rapid Fracture Results in Air at 21C

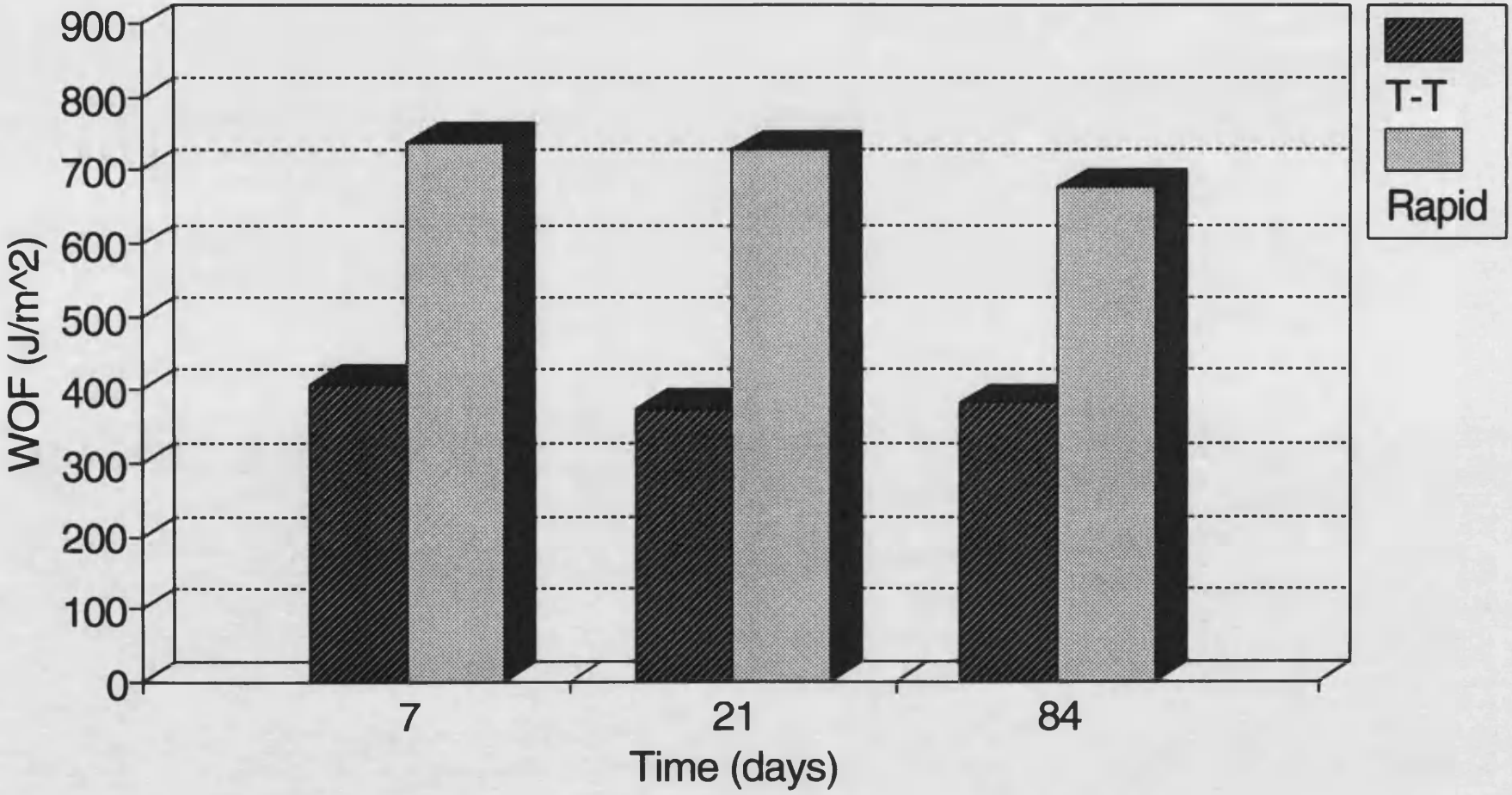


Figure 5.10 : WOF Results versus Rapid Fracture Results in Air at 37C

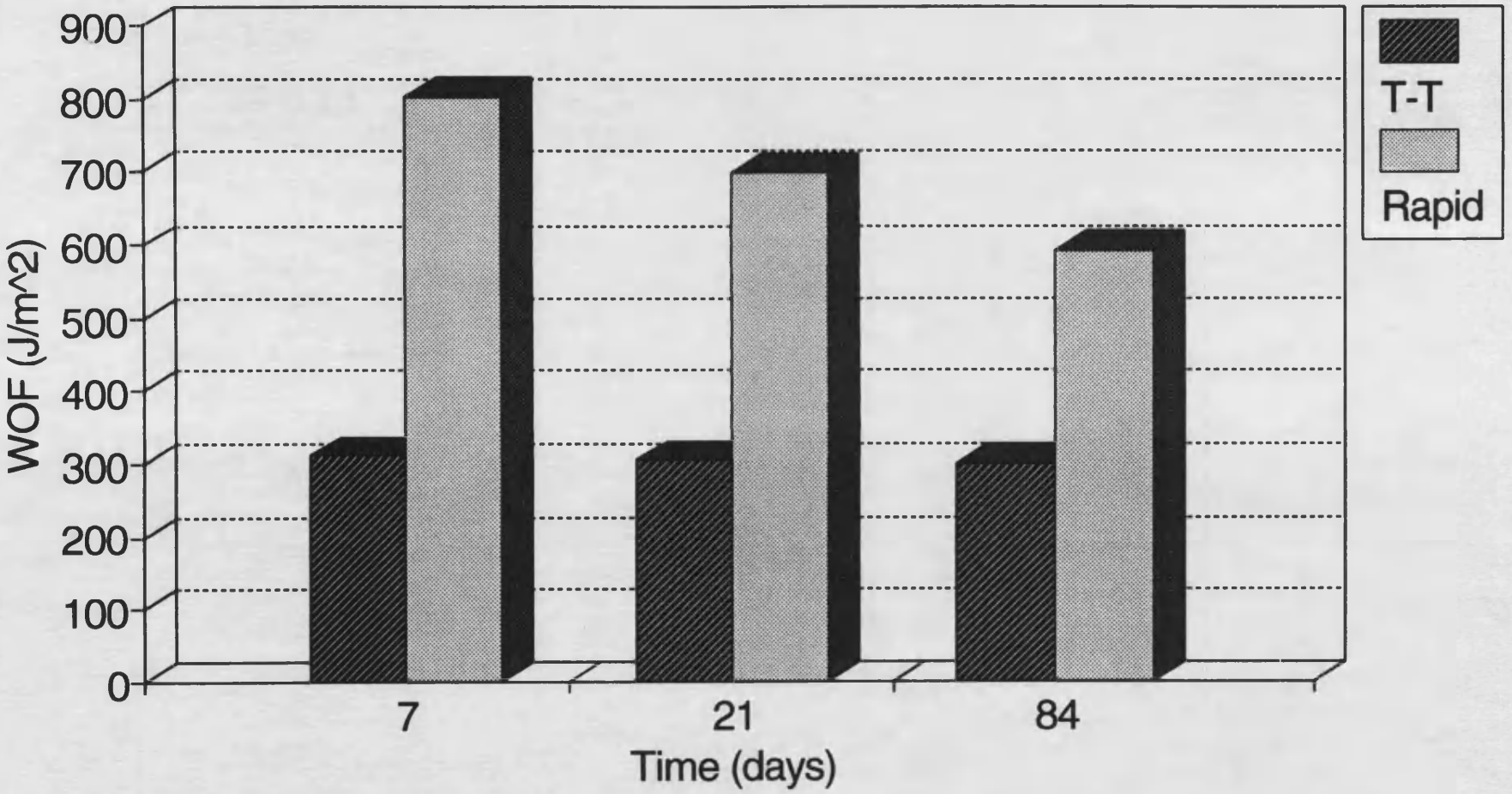


Figure 5.11 : WOF Results versus Rapid Fracture Results in Water at 21C

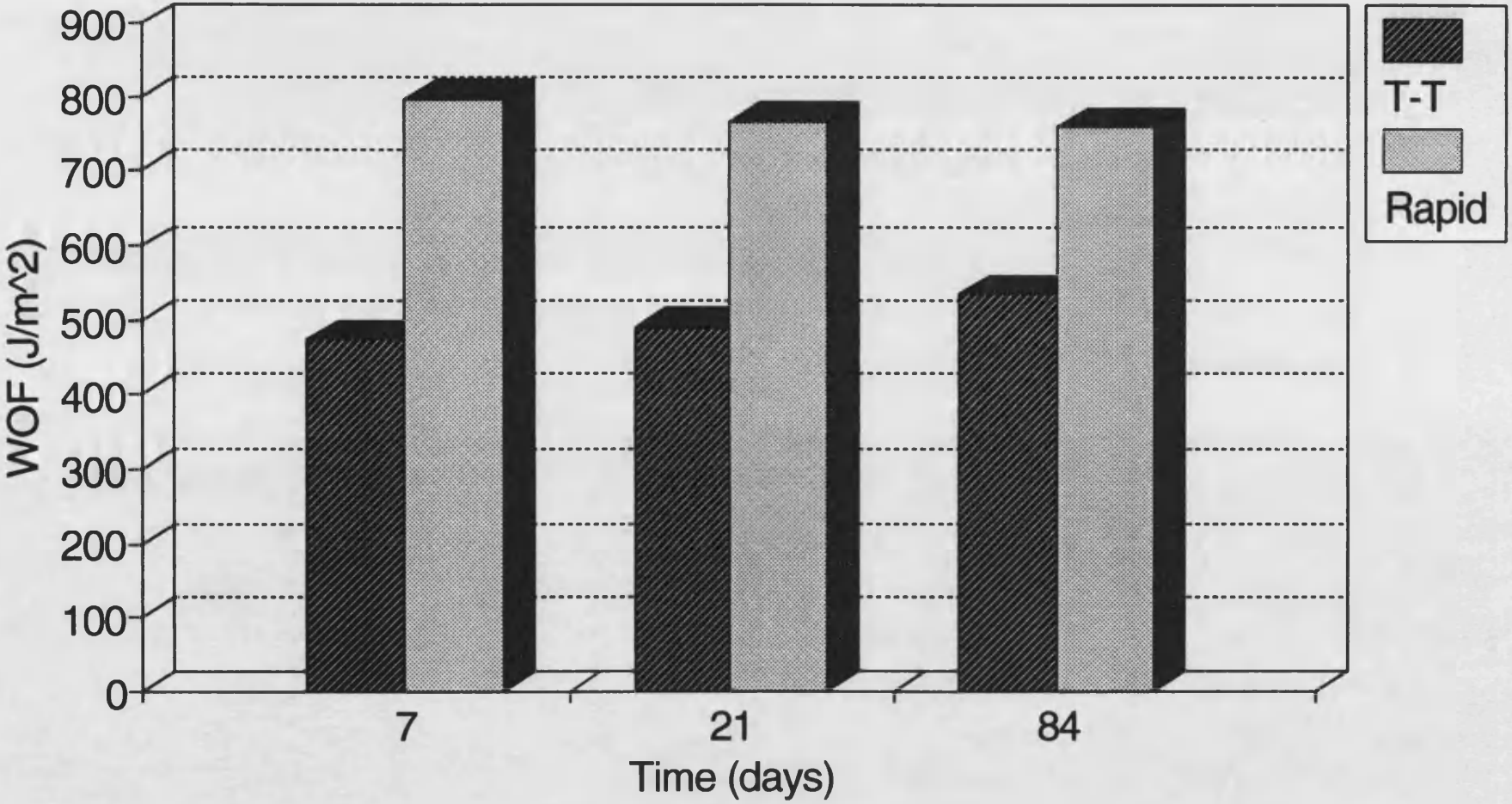


Figure 5.12 : WOF Results versus Rapid Fracture Results in Water at 37C

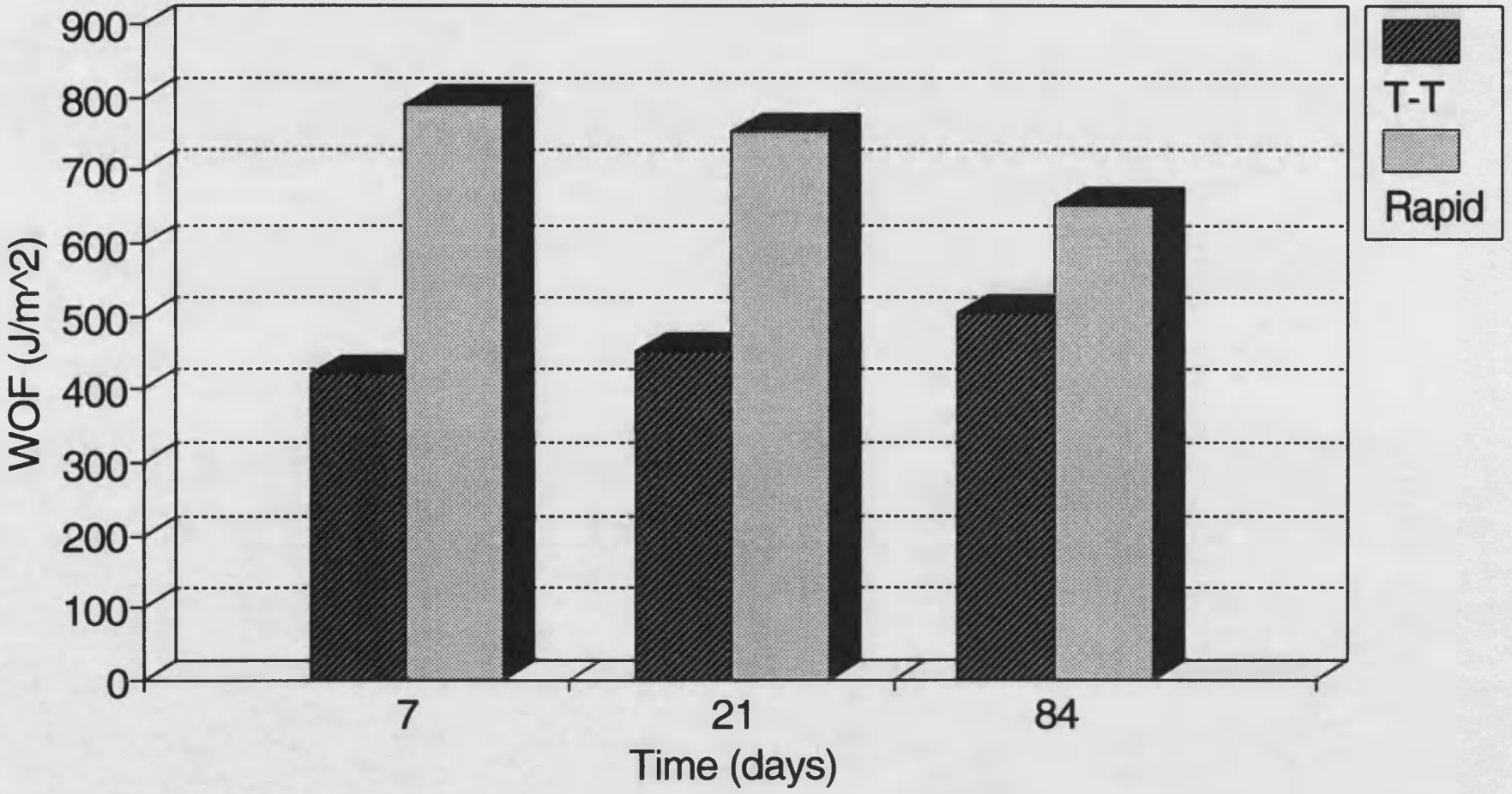


Figure 5.13 : WOF Results versus Rapid Fracture Results in Ringer's at 21C

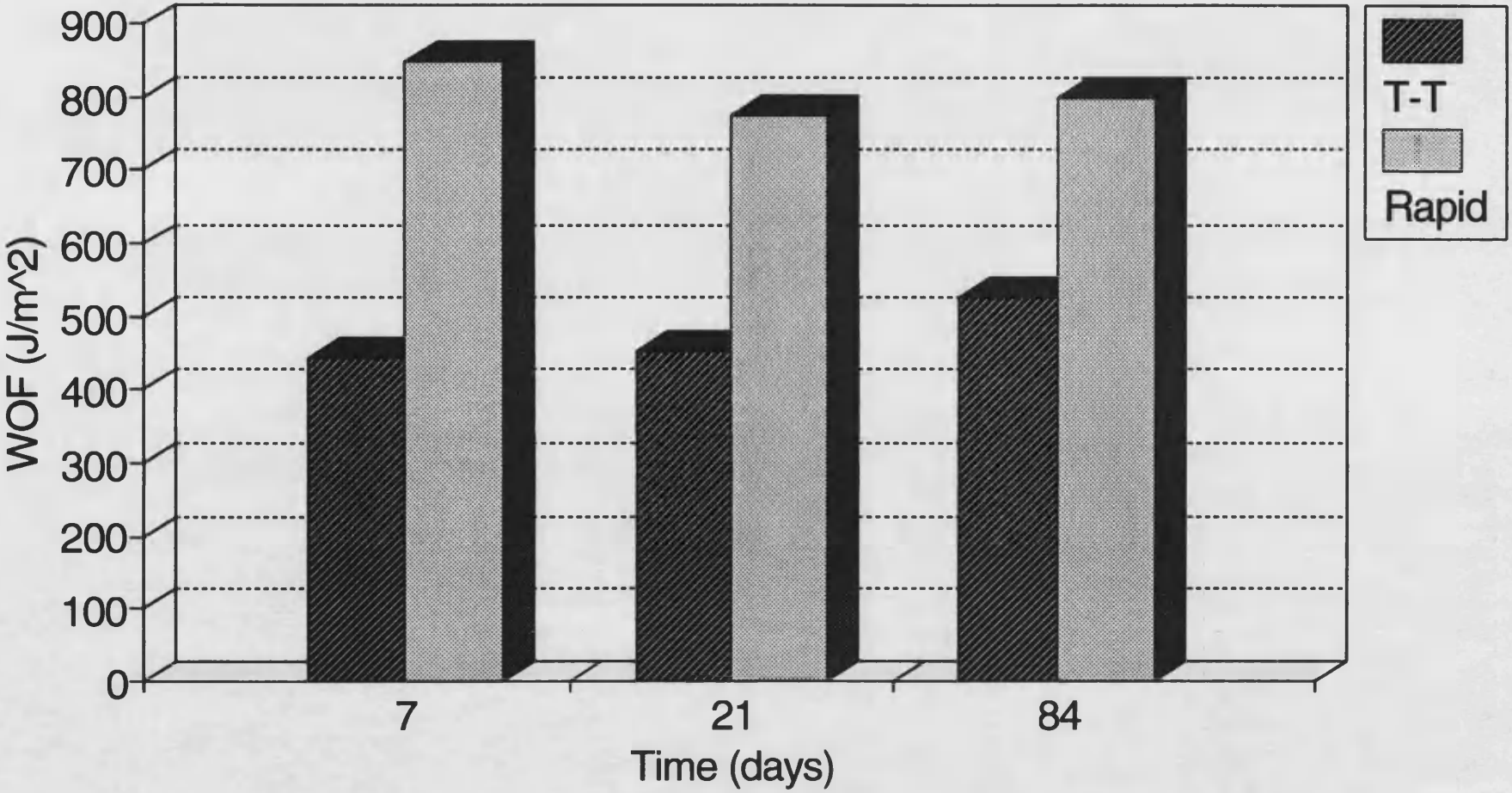


Figure 5.14 : WOF Results versus Rapid Fracture Results in Ringer's at 37C

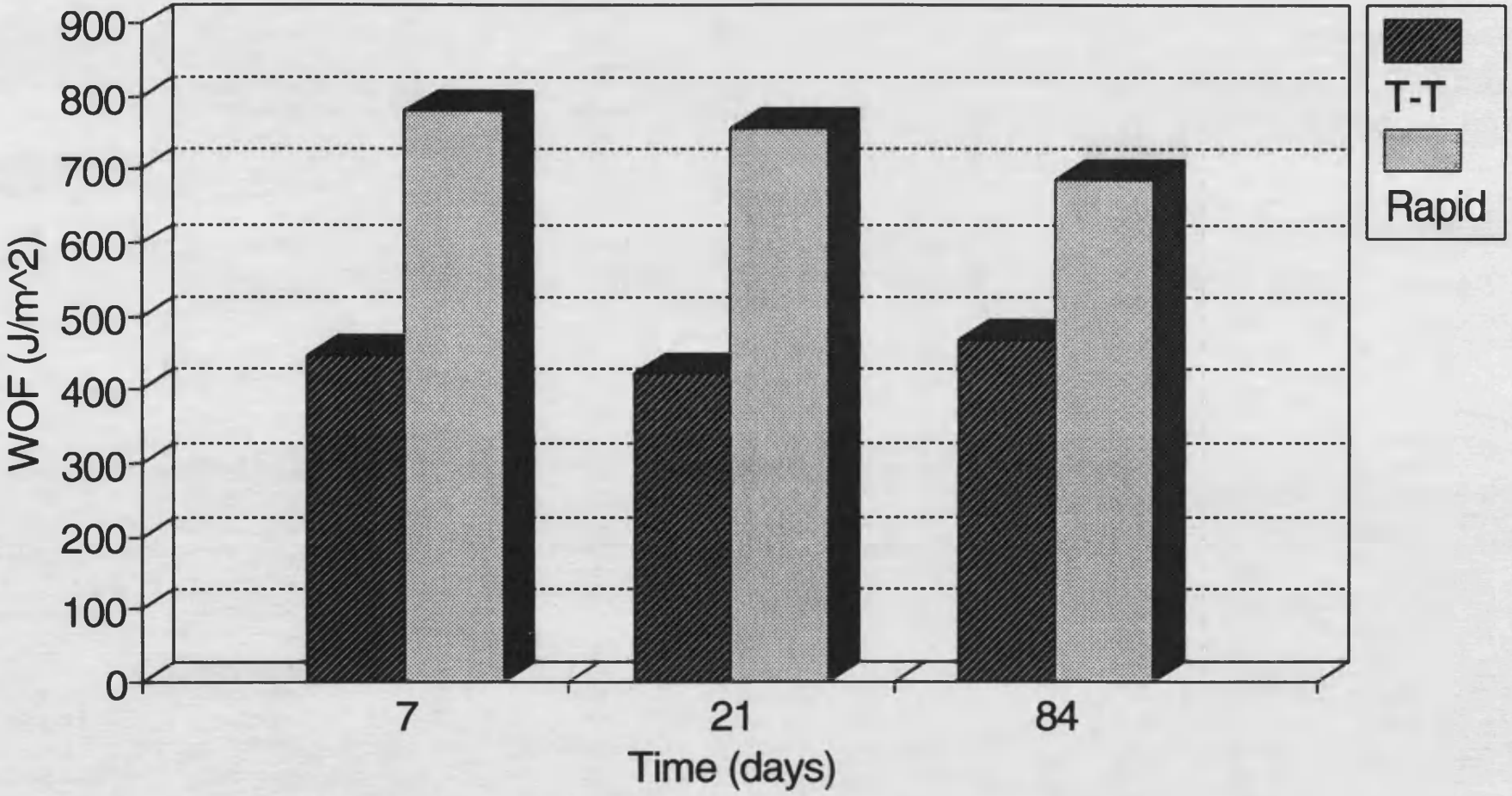


Figure 5.15 : WOF Results versus Rapid Fracture Results in Lipid at 21C

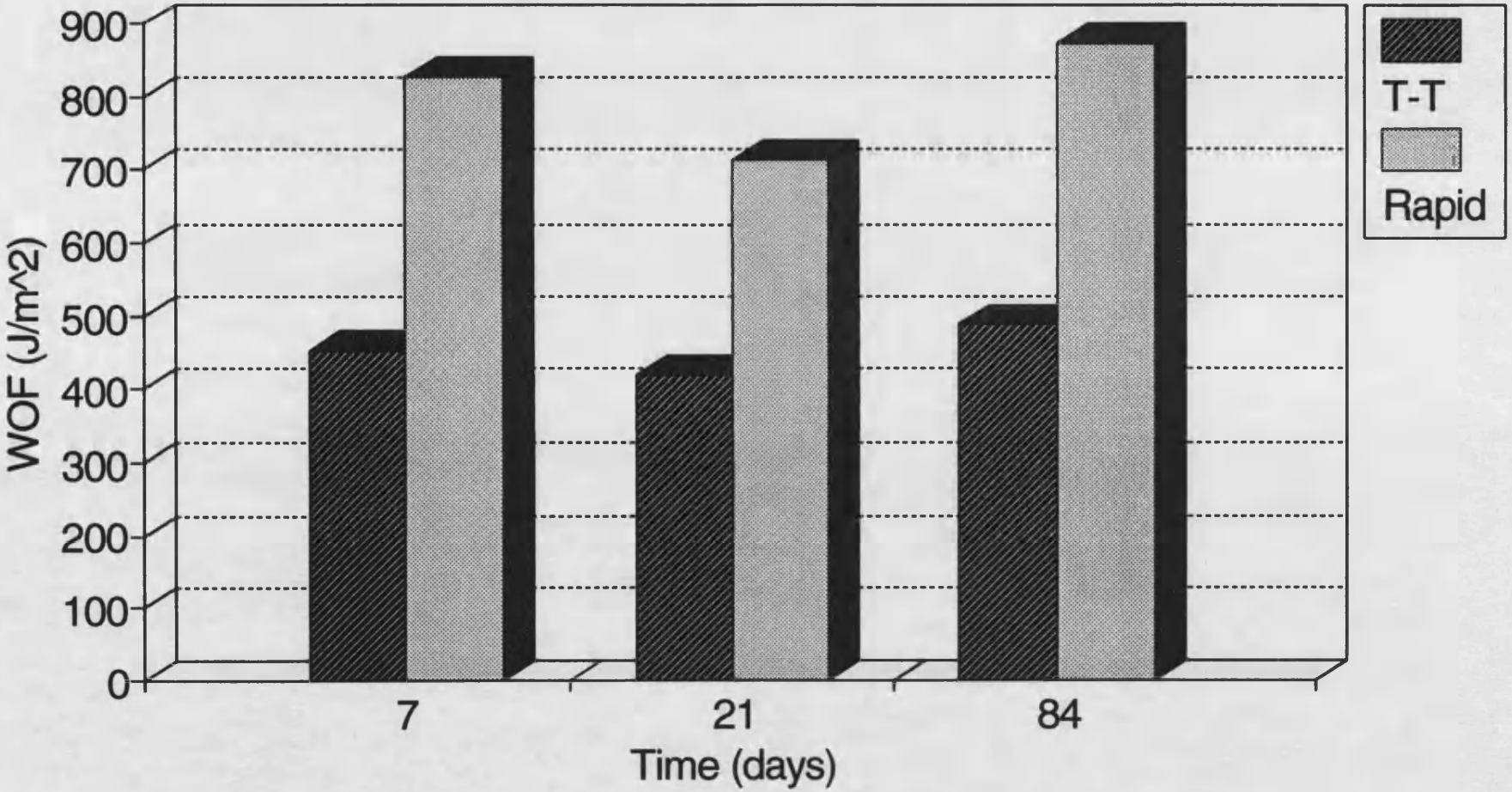
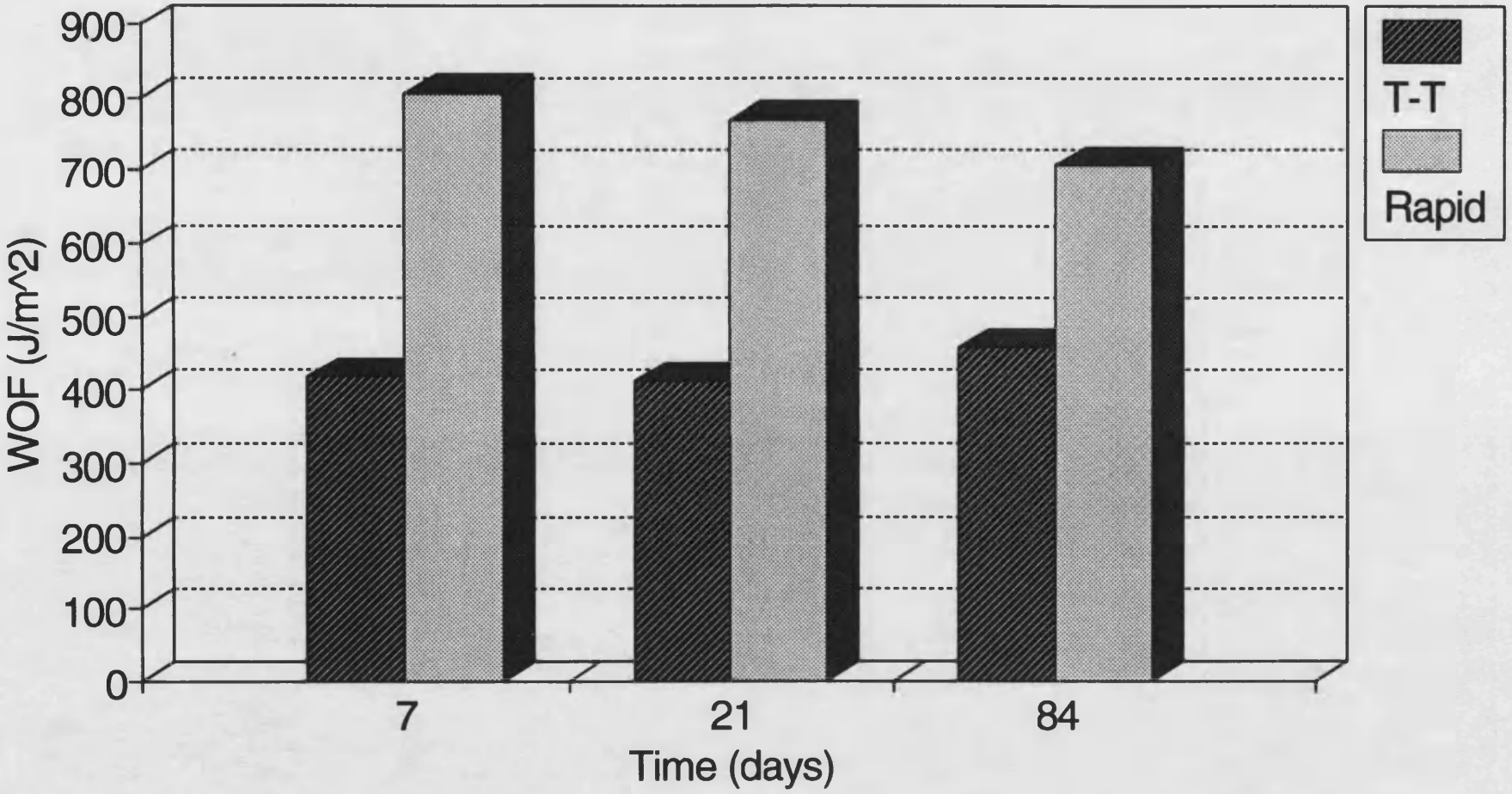


Figure 5.16 : WOF Results versus Rapid Fracture Results in Lipid at 37C



6. ENVIRONMENTAL INGRESS

6.1 Environmental Ingress Results

6.1.1 Details of the Presentation of the Results

Unlike the WOF fracture tests where measurements were made locally in one plane, and any gross porosity in this plane resulted in an unrepresentatively low WOF value, the environmental ingress occurred over the whole sample. Thus for this series of experiments, any local variations in porosity content were averaged over the rest of the sample. Hence all the specimens studied were assumed to be representative, and all the measurements made were used in calculating the mean results and standard deviations.

The tables of results give the number of samples weighed, mean percentage weight change, standard deviation, and 95% confidence interval (95%CI) for both normal and fully cured cement samples for different storage periods in the eight environments.

The environmental ingress results are also shown graphically on twelve separate graphs, six showing the results for normal cement (Figures 6.1 - 6.6) and the other six showing those for fully cured cement (Figures 6.7 - 6.12). The six graphs for each of the two materials are plotted as x-y graphs on a true time x-axis, with percentage weight change on the y-axis. The symbols on all the graphs represent the mean percentage weight change for that particular storage period in the environment concerned. Again the standard deviations are not shown on the graphs to allow easier comparison of the data, but the statistical analysis of the results is discussed in Appendix C, with the 95%CI being plotted on Figures C.31 - C.50.

The first four graphs (Figures 6.1 - 6.4 and 6.7 - 6.10) show the weight changes for each storage period in the four different media. Each graph corresponds to one of the storage media and shows the weight changes at both 21°C and 37°C. These graphs allowed the effect of the environmental ingress of each of the media to be quantified,

and enabled the results for the two different storage temperatures to be compared.

The final pair of graphs (Figures 6.5 - 6.6 and 6.11 - 6.12) show the results for each of the two storage temperatures, with the four different media shown on each graph. This was to allow the comparison of the results for the four different storage media.

6.1.2 Results for Normal Cement

The weight change results from the study of the environmental ingress into samples of normal cement are given in Tables 6.1 - 6.8. The mean weight changes are also plotted against storage time in the various environments in Figures 6.1 - 6.6.

Figures 6.1 - 6.4 show the environmental ingress results for air, water, Ringer's, and lipid respectively. It can be seen from these graphs that whilst samples stored in air lost weight, those stored in the fluids gained weight over the time periods studied. The samples stored in air at both temperatures lost a significant amount of weight over the first 50 days. Then there was a significant increase in weight over the next 50 days, after which the weight change stabilised to a steady value (see Figures 6.1 and C.31). It can also be seen that samples stored at 37°C experienced significantly greater weight losses than those stored at 21°C. The maximum weight loss of the samples stored in air at 21°C was approximately 0.24% (0.004g), and that of samples at 37°C was 0.47% (0.008g). For samples stored in the three fluid media (Figures 6.2 - 6.4) there was a significant increase in weight with time, although the weight gains between any two adjacent time periods were not significant. There was also a tendency for samples stored at 37°C to gain more weight than those stored at 21°C, although this trend was only significant for half the time periods studied (see also Figures C.32 - C.34). The weight gains appeared to have stabilised after storage in the fluids for approximately 150 days giving an equilibrium weight gain of approximately 2.2% (0.035g).

The effects of the four storage media at 21°C and 37°C are shown in Figures 6.5 and 6.6 respectively. From these graphs the differences between storage of samples in air and storage in the fluids can clearly be seen, the air stored samples losing weight as those stored in fluids gained weight. Although from Figures 6.5 and 6.6 it appeared that samples stored in Ringer's solution gained less weight than those stored in water and lipid, there was generally no significant difference between the percentage weight gains for any of the three fluids studied (see also Figures C.37 - C.40).

6.1.3 Results for Fully Cured Cement

The environmental ingress results for samples of fully cured cement are given in Tables 6.9 - 6.16, and are presented graphically in Figures 6.7 - 6.12.

Figures 6.7 - 6.10 show the mean percentage weight changes for samples stored in air, water, Ringer's, and lipid respectively. It can be seen from these graphs that samples stored in all of the four media gained a significant amount of weight over the time period studied, although again the increases in weight between any two adjacent time periods were not significant. Figures 6.7 and C.41 show that the weight gain for samples stored in air at 21°C was significantly greater than for those at 37°C. It can also be seen that for samples stored at 37°C the weight gain had stabilised after approximately 100 days, giving a maximum weight gain of approximately 0.21% (0.003g). Whereas samples stored at 21°C were still gaining significant amounts of weight after storage for 150 days, giving an equilibrium weight gain in excess of 0.52% (0.008g). From Figures 6.8 - 6.10 it can be seen that storage of samples in all three of the fluid media gave similar results. In all three fluids samples which were stored at 37°C for short periods (up to approximately 70 days) had gained significantly more weight than those stored at 21°C. However, after storage for 89 days, there was no significant difference between the weight gains of samples stored at either temperature (see also Figures C.42 - C.44). The weight gains for all three fluid media

at both temperatures appeared to have stabilised by 150 days of storage, giving an equilibrium weight gain of approximately 2.4% (0.038g).

Figures 6.11 and 6.12 show the environmental ingress results for all four storage media at 21°C and 37°C respectively. It can be seen from these graphs that although samples stored in all of the four media gained weight over the time period studied, those stored in the fluids gained significantly more weight than those stored in air (see also Figures C.45 and C.46). There generally appeared to be no significant difference between the weight gains for samples stored in any of the three fluids, although in some isolated cases samples stored in water gained significantly more weight than those stored in Ringer's and significantly less than those stored in lipid (see Figures C.47 - C.50, and Appendix C for details).

6.2 Discussion of Environmental Ingress

6.2.1 Normal Cement

Reviewing the literature concerning the water absorption of bone cements and dental acrylics it appears that, since the two are chemical very similar, there is little difference between the fluid uptake of the two materials. Hence in this section it is valid to makes comparisons between the environmental ingress into bone cements and that into dental resins.

6.2.1.1 Effect of Storage Conditions

It was shown in section 6.1.2 that samples of normal cement which were stored in air lost weight with time, which was probably due to the loss of residual monomer from within the cement. Lautenschlager, Stupp and Keller (1984) and Bayne, Lautenschlager, Greener and Meyer (1977) reported that the largest and most rapid

monomer losses occurred during mixing and the setting exotherm, and that little monomer was lost in the period between the end of mixing and the beginning of the exotherm. Both groups of authors also reported that once the cement had set there was minimal monomer loss, which is in agreement with our results. In this study there was a maximum weight loss of 0.23% (0.0007g) at 21°C and 0.47% (0.0014g) at 37°C after storage in air for approximately 50 days at both of the temperatures. This may not correspond to the actual weight of monomer lost however. After the maximum weight loss had been achieved at 50 days storage, there was a gradual 0.05% increase in the weight of the samples stored at 37°C and a 0.11% increase at 21°C over the following 50 day period. This weight increase was attributed to the samples absorbing water vapour from the atmosphere, so this would indicate that the actual monomer losses were greater than the maximum weight losses (0.23% at 21°C and 0.47% at 37°C). However, this assumes that the weight losses are due solely to evaporation of residual monomer from within the cement mass. There may be other volatile residual substances within the cement which also evaporate during storage in air, which would result in monomer losses which were less than the maximum weight losses. The actual amounts of residual monomer which were lost were evaluated using gas chromatography, and the results are given in section 7.

In a study to monitor the monomer loss from bone cement dough due to evaporation during mixing, Lee and Ling (1975) also found that the most significant losses occurred during mixing, and that within 2.5 - 3 minutes after mixed had ceased the monomer loss had reached a steady level which was maintained until polymerisation. Their value for the weight of monomer lost over a 30 second period as the cement was setting (9-10 minutes after mixing) was approximately 0.01g (assuming that a full pack of cement, 68g, was used for each weighing, then this corresponds to 0.015%). The weight losses from our study are clearly much lower (approximately 0.1% over the first two day period) than the values quoted by Lee and Ling (1975), due to our study being performed on cement from 30 minutes after curing, rather than as it was

curing, when one would expect the monomer losses to be much less. Wroblewski (1977) reported a 0.3% drop in weight for a standard pack of cement as it was setting and only an average change in weight of 0.02% over a 6 week period after the cement had set. This weight change was considerably lower than that observed in our study, which was a 0.24% loss in weight for samples stored in air at 21°C for 43 days. The specimens produced by Wroblewski (1977) were, however, approximately four times the size of those produced for our study, since Wroblewski (1977) divided a standard mix of cement into 6 lumps, and 16 rectangular beams were produced from two-thirds of a pack of cement in our study. Hence there was probably less surface area to volume available from which the volatile substances could evaporate in Wroblewski's (1977) tests than in our environmental ingress tests.

It was also shown in section 6.1.2 that samples stored in the three fluid media all gained weight with time, indicating that environmental ingress was occurring. Within experimental error there appeared to be no difference between the weight gains for the fluids, thus indicating that the fluid uptake was the same for all of the three liquid media. It was also apparent that there was little difference between the environmental ingress for samples stored at 37°C and those stored at 21°C. Several other authors have also reported on the fluid absorption of acrylic dental resins and bone cements, and the results of their papers are summarised below.

Wroblewski (1977) reported an average weight gain of 0.5% after storage of his samples of cement in normal saline for 2 weeks which was considerably lower than that found in our study (1.14% after 15 days in Ringer's solution at 21°C). This again reflected the smaller ratio of surface area to volume of the author's specimens when compared to ours. De Wijn, Slooff and Driessens (1975) reported water absorption percentages of 1.2-1.5% for 0.5mm thick samples of bone cement which had been stored in water at 37°C for 24 hours. The weight gains obtained in our study were 0.71%, 0.74% and 0.94% for samples stored for 2 days at 37°C in water, Ringer's and

lipid respectively. The samples produced by the above authors were considerably thinner than those used in our study, 0.5mm and 5mm respectively. Hence the former samples would become saturated with water much more quickly than would the WOF type specimens used in our study. Kusy (1978) evaluated the water absorption of mechanical test specimens of cement and reported similar values to those found in our study, probably because the two specimens were of a similar size and shape. Kusy gave a value of 2.1% for the absorption of Simplex P specimens which had been stored in water at 37° for 10 months, which is a little less than our value of 2.5% after storage in water at 37°C for 171 days. It has been reported elsewhere (Lautenschlager, Stupp and Keller, 1984) that water absorption weight increases are dependent upon the size and shape of the specimens, and on the area of the surface which is exposed to the water. Also Braden (1964) has shown that the thickness of the specimen markedly affects the water absorption of acrylic resins, which would explain the variation in the water absorption results reported by the various groups.

Braden (1964) showed that for dental resin specimens which were 1.04mm and 0.635mm thick, the equilibrium water absorption (saturation) occurred after approximately 14 days at 22.5°C and 6 days at 37.4°C. Bevan and Earnshaw (1968) found that for specimens of dental acrylic 0.2cm thick stored in water at 37°C, the equilibrium water concentration was reached in approximately 15 days, and Smith (1961) showed that for specimens 0.3mm thick stored in water at 20°C and 37°C, saturation occurred after 70 - 80 days. All these results showed saturation of the specimens to occur in a much shorter time than observed in our study, although the specimens used were much thinner than our specimens. Using a diffusion coefficient of $2x10^{-8}cm^2sec^{-1}$ (an average of the diffusion coefficients at 21°C and 37°C), Braden (1964) showed that for specimens 5mm thick 99.9% saturation would occur after approximately 120 days in water. This is in good agreement with our results, as the environmental ingress graphs (Figures 6.5 and 6.6) began to stabilise after approximately 140 days.

6.2.2 Fully Cured Cement

It was shown in section 6.1.3 that storage of fully cured cement samples in all four of the media, including air, resulted in weight gains. This indicated that environmental ingress of the fluids into the fully cured cement was occurring in a similar manner to that previously discussed with the normal cement. However, unlike the samples of normal cement, fully cured cement samples gained weight when they were stored in air. This was attributed to the removal of any water from the cured cement during the heat treatment, and a subsequent re-hydration of the material as it absorbed moisture from the atmosphere. Smith (1961) has shown that heat treated dental resins which were stored in air gradually gained approximately 0.5% in weight due to the absorption of water vapour from the atmosphere.

The environmental ingress into samples of fully cured bone cement was very similar to that of normal cement, which indicates that it is unlikely that the residual monomer is leaching out from the normal cement in large quantities. This is supported by the gas chromatography analysis of the amount of residual monomer present within the bone cement given in section 7, except lipid. If there had have been significant monomer losses then a complex curve would have been obtained, which was a combination of residual monomer losses and fluid absorption.

It has been shown by Bevan and Earnshaw (1968) and Smith (1961) that the ingress of water into dental acrylics does not vary with molecular weight, so even if the fully cured cement has a higher molecular weight than the normal material, it is unlikely that any differences between the environmental ingress for the two types of cements would have been observed.

6.3 Summary of Environmental Ingress

It has been shown that samples of bone cement which were stored in air lost residual monomer due to evaporation, and absorbed small amounts of water vapour from the atmosphere. Samples which were stored in the fluid media all experienced environmental ingress and over a 6 month period the samples increased in weight by approximately 2-3%. There appeared to be no differences between the weight gains of the normal and heat treated cement. Also no differences were identified between the environmental ingress of the different storage media at the two temperatures studied.

The effect of the environmental ingress would be firstly to cause the cement to swell, which may improve the mechanical interlock with the bone *in vivo*. The second effect of the absorption of the fluids would be to plasticise the cement, which would decrease the elastic modulus and thus increase the resistance to crack growth.

Table 6.1 : Weight Change Results for Normal Bone Cement Samples Stored in Air 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	-0.106	0.019	–0.11±0.02
3 days	6	-0.127	0.018	–0.13±0.02
4 days	6	-0.147	0.019	–0.15±0.02
5 days	6	-0.144	0.024	–0.14±0.03
6 days	6	-0.165	0.022	–0.17±0.02
9 days	6	-0.188	0.023	–0.19±0.02
12 days	6	-0.192	0.025	–0.19±0.03
15 days	6	-0.204	0.029	–0.20±0.03
18 days	6	-0.215	0.028	-0.22±0.03
21 days	6	-0.218	0.030	-0.22±0.03
25 days	6	-0.231	0.027	-0.23±0.03
31 days	6	-0.242	0.029	-0.24±0.03
43 days	6	-0.237	0.031	-0.24±0.03
50 days	6	-0.238	0.031	-0.24±0.03
59 days	6	-0.244	0.034	-0.24±0.04
74 days	6	-0.194	0.032	-0.19±0.03
92 days	6	-0.165	0.030	-0.17±0.03
103 days	6	-0.150	0.035	-0.15±0.04
128 days	6	-0.122	0.037	-0.12±0.04
149 days	6	-0.120	0.037	–0.12±0.04
171 days	6	-0.119	0.045	–0.12±0.05

Table 6.2 : Weight Change Results for Normal Bone Cement Samples Stored in Air 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	-0.213	0.022	–0.21±0.02
3 days	6	-0.278	0.022	–0.28±0.02
4 days	6	-0.310	0.022	–0.31±0.02
5 days	6	-0.322	0.021	–0.32±0.02
6 days	6	-0.342	0.021	–0.34±0.02
9 days	6	-0.378	0.023	–0.38±0.02
12 days	6	-0.398	0.024	–0.40±0.03
15 days	6	-0.417	0.022	–0.42±0.02
18 days	6	-0.431	0.025	-0.43±0.03
21 days	6	-0.435	0.025	-0.44±0.03
25 days	6	-0.449	0.026	-0.45±0.03
31 days	6	-0.456	0.015	-0.46±0.02
43 days	6	-0.466	0.017	-0.47±0.02
50 days	6	-0.468	0.017	-0.47±0.02
59 days	6	-0.461	0.018	-0.46±0.02
74 days	6	-0.445	0.018	-0.45±0.02
92 days	6	-0.438	0.015	-0.44±0.02
103 days	6	-0.416	0.020	-0.42±0.02
128 days	6	-0.425	0.019	-0.43±0.02
149 days	6	-0.430	0.019	–0.43±0.02
171 days	6	-0.447	0.020	–0.45±0.02

Table 6.3 : Weight Change Results for Normal Bone Cement Samples Stored in Water 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.657	0.083	0.66±0.09
3 days	6	0.839	0.182	0.84±0.19
4 days	6	0.941	0.175	0.94±0.18
5 days	6	0.904	0.156	0.90±0.16
6 days	6	0.923	0.119	0.92±0.12
9 days	6	1.033	0.138	1.03±0.14
12 days	6	1.101	0.123	1.10±0.13
15 days	6	1.184	0.162	1.18±0.17
18 days	6	1.247	0.151	1.25±0.16
21 days	6	1.306	0.165	1.31±0.17
25 days	6	1.350	0.134	1.35±0.14
31 days	6	1.410	0.130	1.41±0.14
43 days	6	1.520	0.075	1.52±0.08
50 days	6	1.612	0.154	1.61±0.16
59 days	6	1.675	0.179	1.68±0.19
74 days	6	1.760	0.112	1.76±0.12
92 days	6	1.873	0.165	1.87±0.17
103 days	6	1.888	0.147	1.89±0.15
128 days	6	2.030	0.178	2.03±0.19
149 days	6	2.063	0.199	2.06±0.21
171 days	6	2.146	0.235	2.15±0.25

Table 6.4 : Weight Change Results for Normal Bone Cement Samples Stored in Water 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.717	0.266	0.71±0.28
3 days	6	0.922	0.229	0.92±0.24
4 days	6	0.982	0.227	0.98±0.24
5 days	6	1.038	0.222	1.04±0.23
6 days	6	1.100	0.207	1.10±0.22
9 days	6	1.229	0.198	1.23±0.21
12 days	6	1.352	0.186	1.35±0.20
15 days	6	1.589	0.199	1.59±0.21
18 days	6	1.692	0.224	1.69±0.24
21 days	6	1.776	0.250	1.78±0.26
25 days	6	1.895	0.282	1.90±0.30
31 days	6	1.930	0.314	1.93±0.33
43 days	6	2.044	0.338	2.04±0.35
50 days	6	2.084	0.362	2.08±0.38
59 days	6	2.140	0.391	2.14±0.41
74 days	6	2.239	0.417	2.24±0.44
92 days	6	2.302	0.426	2.30±0.45
103 days	6	2.331	0.434	2.33±0.46
128 days	6	2.383	0.443	2.38±0.46
149 days	6	2.480	0.441	2.48±0.46
171 days	6	2.523	0.193	2.52±0.20

Table 6.5 : Weight Change Results for Normal Bone Cement Samples Stored in Ringer's 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.668	0.108	0.67±0.11
3 days	6	0.817	0.106	0.82±0.11
4 days	6	0.817	0.027	0.82±0.03
5 days	6	0.828	0.022	0.83±0.02
6 days	6	0.865	0.040	0.87±0.04
9 days	6	0.955	0.036	0.96±0.04
12 days	6	1.013	0.033	1.01±0.03
15 days	6	1.139	0.101	1.14±0.11
18 days	6	1.163	0.048	1.16±0.05
21 days	6	1.208	0.078	1.21±0.08
25 days	6	1.292	0.119	1.29±0.12
31 days	6	1.314	0.088	1.31±0.09
43 days	6	1.409	0.084	1.41±0.09
50 days	6	1.473	0.096	1.47±0.10
59 days	6	1.496	0.106	1.50±0.11
74 days	6	1.560	0.105	1.56±0.11
92 days	6	1.646	0.121	1.65±0.13
103 days	6	1.661	0.139	1.66±0.15
128 days	6	1.687	0.139	1.69±0.15
149 days	6	1.713	0.147	1.71±0.15
171 days	6	1.728	0.127	1.73±0.13

Table 6.6 : Weight Change Results for Normal Bone Cement Samples Stored in Ringer's 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.740	0.108	0.74±0.11
3 days	6	0.890	0.049	0.89±0.05
4 days	6	0.936	0.059	0.94±0.06
5 days	6	1.039	0.028	1.04±0.03
6 days	6	1.064	0.048	1.06±0.05
9 days	6	1.192	0.038	1.19±0.04
12 days	6	1.235	0.018	1.24±0.02
15 days	6	1.343	0.038	1.34±0.04
18 days	6	1.354	0.031	1.35±0.03
21 days	6	1.389	0.045	1.39±0.05
25 days	6	1.484	0.077	1.48±0.08
31 days	6	1.505	0.057	1.51±0.06
43 days	6	1.684	0.106	1.68±0.11
50 days	6	1.720	0.137	1.72±0.14
59 days	6	1.760	0.160	1.76±0.17
74 days	6	1.768	0.156	1.77±0.16
92 days	6	1.801	0.169	1.80±0.18
103 days	6	1.836	0.172	1.84±0.18
128 days	6	1.834	0.192	1.83±0.20
149 days	6	1.862	0.201	1.86±0.21
171 days	6	1.915	0.195	1.92±0.20

Table 6.7 : Weight Change Results for Normal Bone Cement Samples Stored in Lipid 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.962	0.175	0.96±0.18
3 days	6	1.128	0.239	1.13±0.25
4 days	6	1.118	0.332	1.12±0.35
5 days	6	1.193	0.318	1.19±0.33
6 days	6	1.022	0.185	1.02±0.19
9 days	6	1.221	0.402	1.22±0.42
12 days	6	1.235	0.251	1.24±0.26
15 days	6	1.341	0.149	1.34±0.16
18 days	6	1.371	0.217	1.37±0.23
21 days	6	1.402	0.165	1.40±0.17
25 days	6	1.554	0.296	1.55±0.31
31 days	6	1.583	0.202	1.58±0.21
43 days	6	1.692	0.207	1.69±0.22
50 days	6	1.722	0.209	1.72±0.22
59 days	6	1.754	0.152	1.75±0.16
74 days	6	1.831	0.079	1.83±0.08
92 days	6	1.939	0.290	1.94±0.30
103 days	6	1.949	0.267	1.95±0.28
128 days	6	2.179	0.578	2.18±0.61
149 days	6	2.207	0.728	2.21±0.76
171 days	6	2.249	0.745	2.25±0.78

Table 6.8 : Weight Change Results for Normal Bone Cement Samples Stored in Lipid 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
2 days	6	0.935	0.068	0.94±0.07
3 days	6	1.195	0.068	1.20±0.07
4 days	6	1.252	0.061	1.25±0.06
5 days	6	1.389	0.069	1.39±0.07
6 days	6	1.367	0.050	1.37±0.05
9 days	6	1.560	0.075	1.56±0.08
12 days	6	1.618	0.089	1.62±0.09
15 days	6	1.706	0.103	1.71±0.11
18 days	6	1.741	0.090	1.74±0.09
21 days	6	1.805	0.052	1.81±0.05
25 days	6	1.847	0.111	1.84±0.12
31 days	6	1.909	0.076	1.91±0.08
43 days	6	2.046	0.041	2.05±0.04
50 days	6	1.963	0.057	1.96±0.06
59 days	6	2.065	0.104	2.07±0.11
74 days	6	2.155	0.162	2.16±0.17
92 days	6	2.124	0.107	2.12±0.11
103 days	6	2.142	0.104	2.14±0.11
128 days	6	2.266	0.102	2.27±0.11
149 days	6	2.327	0.133	2.33±0.14
171 days	6	2.317	0.128	2.32±0.13

Table 6.9 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Air 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.053	0.006	0.05±0.01
2 days	6	0.078	0.005	0.08±0.01
3 days	6	0.089	0.006	0.09±0.01
6 days	6	0.113	0.007	0.11±0.01
9 days	6	0.142	0.009	0.14±0.01
12 days	6	0.160	0.011	0.16±0.01
15 days	6	0.176	0.007	0.18±0.01
18 days	6	0.201	0.010	0.20±0.01
22 days	6	0.214	0.009	0.21±0.01
28 days	6	0.230	0.006	0.23±0.01
40 days	6	0.263	0.005	0.26±0.01
47 days	6	0.283	0.007	0.28±0.01
56 days	6	0.296	0.005	0.30±0.01
71 days	6	0.379	0.007	0.38±0.01
89 days	6	0.425	0.008	0.43±0.01
100 days	6	0.455	0.006	0.46±0.01
125 days	6	0.508	0.007	0.51±0.01
146 days	6	0.522	0.006	0.52±0.01
168 days	6	0.543	0.009	0.54±0.01

Table 6.10 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Air 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.040	0.009	0.04±0.01
2 days	6	0.068	0.005	0.07±0.01
3 days	6	0.076	0.006	0.08±0.01
6 days	6	0.096	0.003	0.10±0.01
9 days	6	0.108	0.004	0.11±0.01
12 days	6	0.114	0.005	0.11±0.01
15 days	6	0.117	0.004	0.12±0.01
18 days	6	0.129	0.005	0.13±0.01
22 days	6	0.130	0.008	0.13±0.01
28 days	6	0.128	0.006	0.13±0.01
40 days	6	0.133	0.005	0.13±0.01
47 days	6	0.139	0.004	0.14±0.01
56 days	6	0.145	0.004	0.15±0.01
71 days	6	0.181	0.004	0.18±0.01
89 days	6	0.193	0.012	0.19±0.01
100 days	6	0.210	0.006	0.21±0.01
125 days	6	0.223	0.008	0.22±0.01
146 days	6	0.218	0.005	0.22±0.01
168 days	6	0.215	0.006	0.22±0.01

Table 6.11 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Water 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.526	0.056	0.53±0.06
2 days	6	0.660	0.019	0.66±0.02
3 days	6	0.707	0.014	0.71±0.01
6 days	6	0.891	0.019	0.89±0.02
9 days	6	1.019	0.035	1.02±0.04
12 days	6	1.145	0.039	1.15±0.04
15 days	6	1.240	0.036	1.24±0.04
18 days	6	1.321	0.030	1.32±0.03
22 days	6	1.416	0.039	1.42±0.04
28 days	6	1.557	0.043	1.56±0.05
40 days	6	1.744	0.032	1.74±0.03
47 days	6	1.827	0.045	1.83±0.05
56 days	6	1.882	0.041	1.88±0.04
71 days	6	2.004	0.050	2.00±0.05
89 days	6	2.111	0.047	2.11±0.05
100 days	6	2.143	0.057	2.14±0.06
125 days	6	2.219	0.060	2.22±0.06
146 days	6	2.256	0.060	2.26±0.06
168 days	6	2.305	0.052	2.31±0.05

Table 6.12 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Water 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.687	0.056	0.69±0.06
2 days	6	0.938	0.072	0.94±0.08
3 days	6	1.018	0.057	1.02±0.06
6 days	6	1.304	0.055	1.30±0.06
9 days	6	1.479	0.064	1.48±0.07
12 days	6	1.633	0.088	1.63±0.09
15 days	6	1.748	0.079	1.75±0.08
18 days	6	1.808	0.087	1.81±0.09
22 days	6	1.892	0.088	1.89±0.09
28 days	6	1.967	0.086	1.97±0.09
40 days	6	2.094	0.089	2.09±0.09
47 days	6	2.134	0.113	2.13±0.12
56 days	6	2.176	0.125	2.18±0.13
71 days	6	2.242	0.143	2.24±0.15
89 days	6	2.297	0.159	2.30±0.17
100 days	6	2.327	0.176	2.33±0.18
125 days	6	2.383	0.203	2.38±0.21
146 days	6	2.416	0.231	2.42±0.24
168 days	6	2.470	0.245	2.47±0.26

Table 6.13 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Ringer's 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.491	0.049	0.49±0.05
2 days	6	0.622	0.035	0.62±0.04
3 days	6	0.665	0.038	0.67±0.04
6 days	6	0.834	0.047	0.83±0.05
9 days	6	0.989	0.055	0.99±0.06
12 days	6	1.099	0.073	1.10±0.08
15 days	6	1.174	0.057	1.17±0.06
18 days	6	1.244	0.060	1.24±0.06
22 days	6	1.370	0.061	1.37±0.06
28 days	6	1.463	0.066	1.46±0.07
40 days	6	1.641	0.067	1.64±0.07
47 days	6	1.707	0.059	1.71±0.06
56 days	6	1.771	0.057	1.77±0.06
71 days	6	1.882	0.054	1.88±0.06
89 days	6	1.961	0.058	1.96±0.06
100 days	6	1.994	0.065	1.99±0.07
125 days	6	2.044	0.073	2.04±0.08
146 days	6	2.061	0.065	2.06±0.07
168 days	6	2.108	0.076	2.11±0.08

Table 6.14 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Ringer's 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.813	0.108	0.81±0.11
2 days	6	0.956	0.089	0.96±0.09
3 days	6	1.133	0.232	1.13±0.24
6 days	6	1.294	0.059	1.29±0.06
9 days	6	1.462	0.056	1.46±0.06
12 days	6	1.599	0.063	1.60±0.07
15 days	6	1.675	0.047	1.68±0.05
18 days	6	1.752	0.064	1.75±0.07
22 days	6	1.820	0.050	1.82±0.05
28 days	6	1.863	0.025	1.86±0.03
40 days	6	1.974	0.042	1.97±0.04
47 days	6	2.015	0.051	2.02±0.05
56 days	6	2.045	0.052	2.05±0.05
71 days	6	2.084	0.075	2.08±0.08
89 days	6	2.128	0.090	2.13±0.09
100 days	6	2.139	0.089	2.14±0.09
125 days	6	2.162	0.089	2.16±0.09
146 days	6	2.175	0.086	2.18±0.09
168 days	6	2.211	0.100	2.21±0.10

Table 6.15 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Lipid 21°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.719	0.092	0.72±0.10
2 days	6	0.882	0.150	0.88±0.16
3 days	6	0.912	0.115	0.91±0.12
6 days	6	1.110	0.074	1.11±0.08
9 days	6	1.252	0.110	1.25±0.12
12 days	6	1.378	0.110	1.38±0.12
15 days	6	1.486	0.114	1.49±0.12
18 days	6	1.587	0.139	1.59±0.15
22 days	6	1.732	0.132	1.73±0.14
28 days	6	1.846	0.151	1.85±0.16
40 days	6	2.030	0.160	2.03±0.17
47 days	6	2.077	0.157	2.08±0.16
56 days	6	2.135	0.146	2.14±0.15
71 days	6	2.270	0.141	2.27±0.15
89 days	6	2.309	0.149	2.31±0.16
100 days	6	2.326	0.140	2.33±0.15
125 days	6	2.396	0.144	2.40±0.15
146 days	6	2.401	0.165	2.40±0.17
168 days	6	2.430	0.133	2.43±0.14

Table 6.16 : Weight Change Results for Fully Cured Bone Cement Samples Stored in Lipid 37°C

Storage Time	No. of Samples	Mean Percentage Increase in Mass	Standard Deviation	95% C.I.
1 day	6	0.860	0.043	0.86±0.05
2 days	6	1.123	0.037	1.12±0.04
3 days	6	1.239	0.068	1.24±0.07
6 days	6	1.503	0.043	1.50±0.05
9 days	6	1.660	0.074	1.66±0.08
12 days	6	1.805	0.096	1.81±0.10
15 days	6	1.936	0.121	1.94±0.13
18 days	6	2.017	0.103	2.02±0.11
22 days	6	2.083	0.115	2.08±0.12
28 days	6	2.152	0.113	2.15±0.12
40 days	6	2.230	0.118	2.23±0.12
47 days	6	2.253	0.096	2.25±0.10
56 days	6	2.323	0.090	2.32±0.09
71 days	6	2.379	0.085	2.38±0.09
89 days	6	2.352	0.085	2.35±0.09
100 days	6	2.406	0.084	2.41±0.09
125 days	6	2.465	0.080	2.47±0.08
146 days	6	2.569	0.071	2.57±0.07
168 days	6	2.621	0.077	2.62±0.08

Figure 6.1 : Weight Losses for Normal Cement in Air

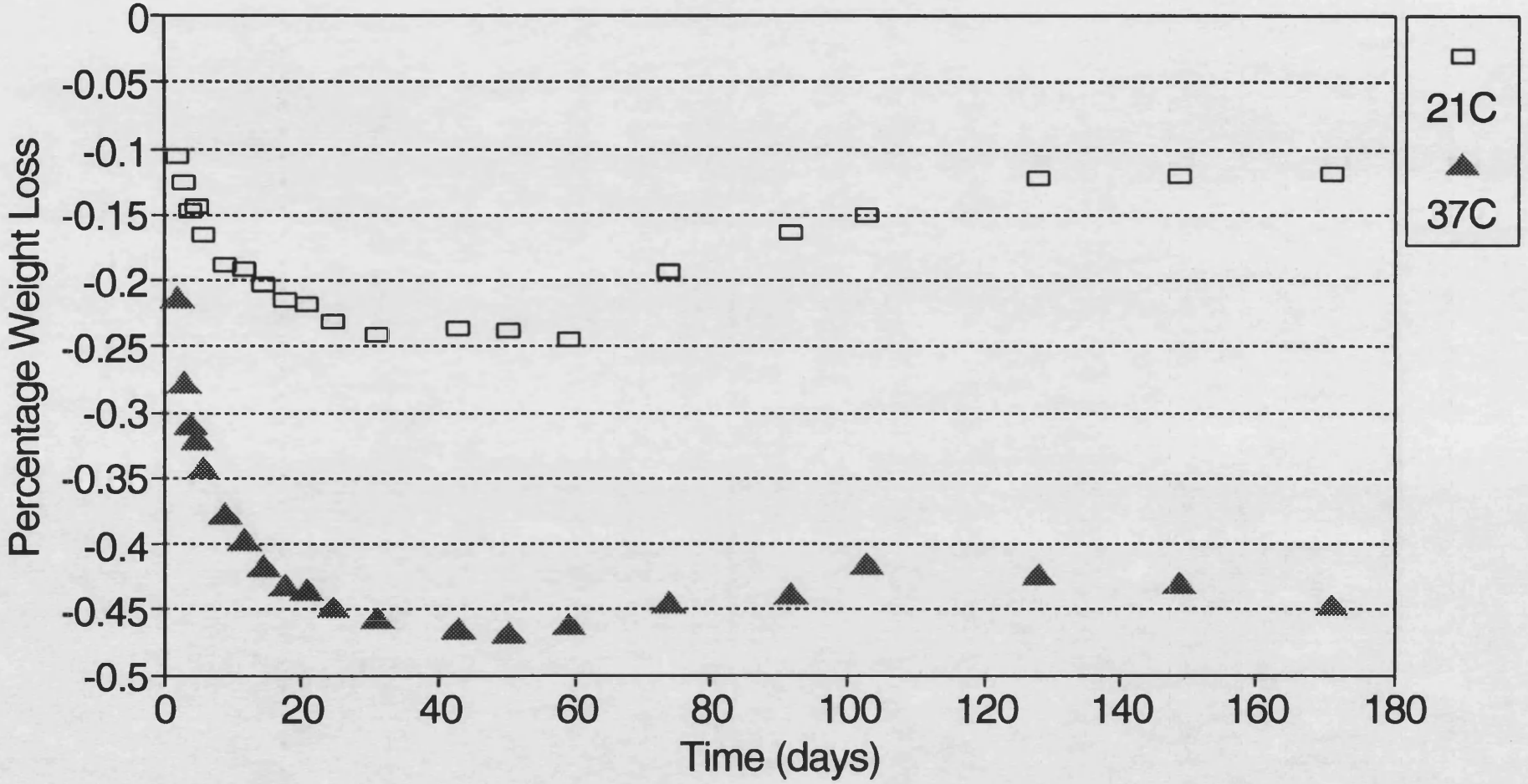


Figure 6.2 : Weight Gains for Normal Cement in Water

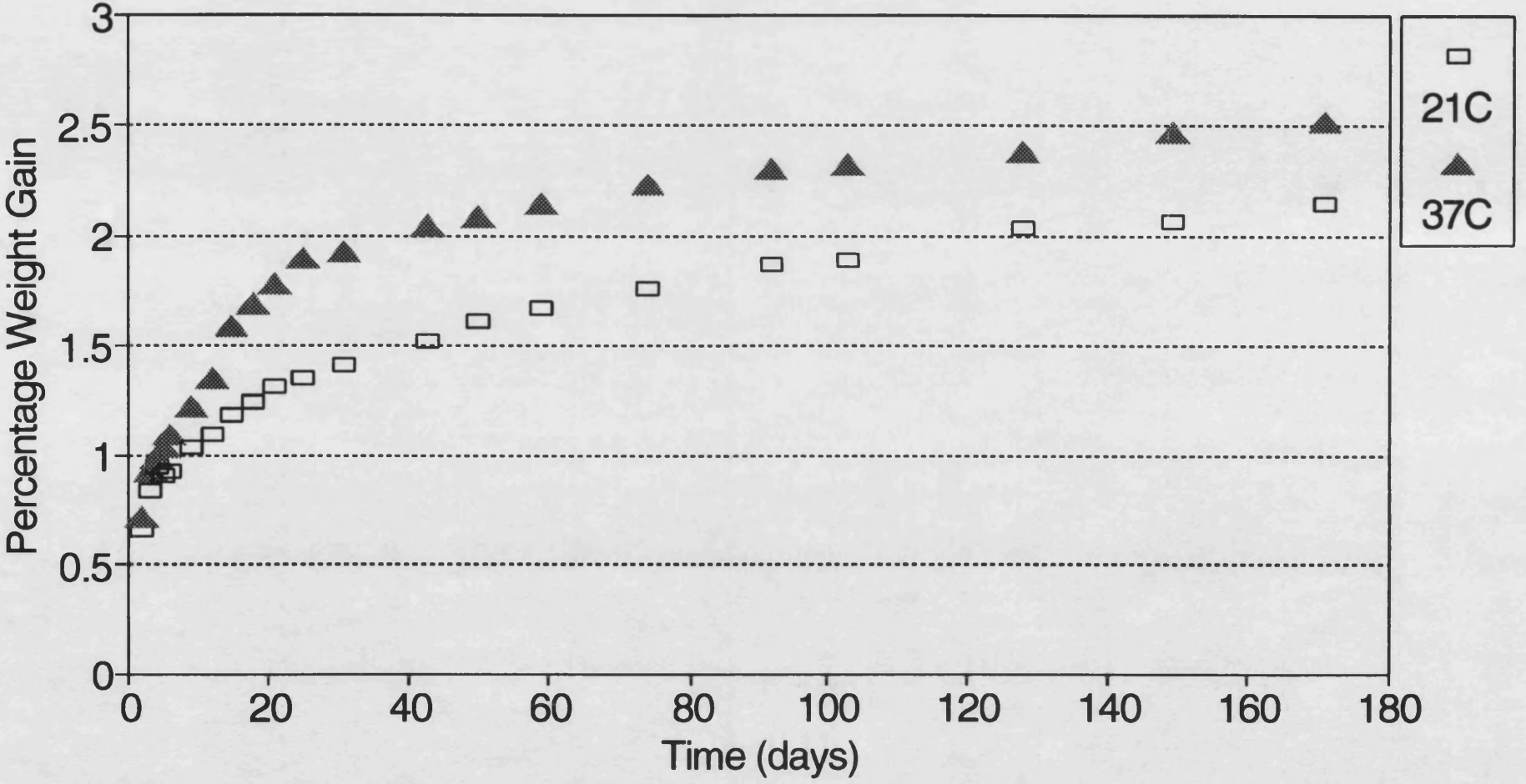


Figure 6.3 : Weight Gains for Normal Cement in Ringer's

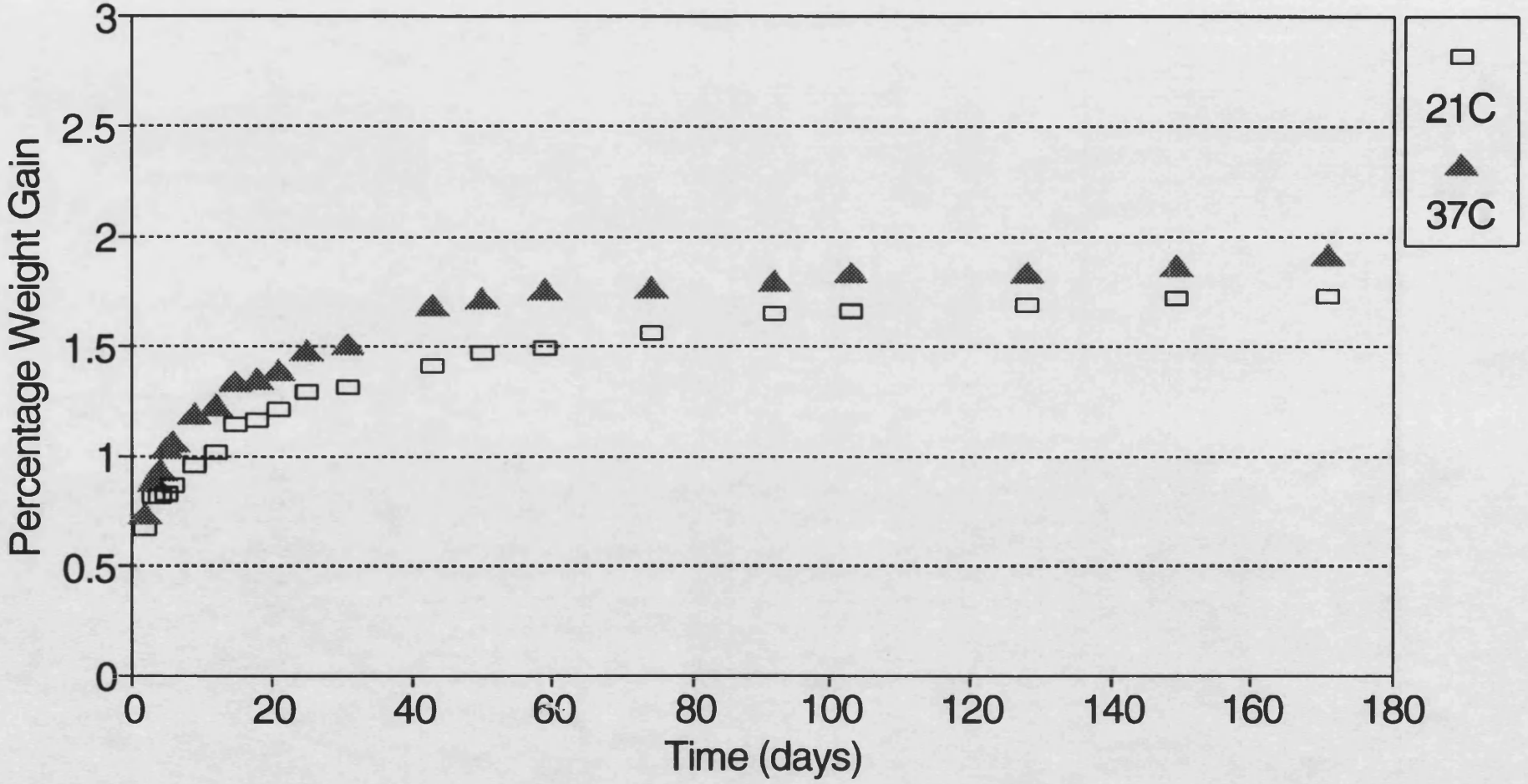


Figure 6.4 : Weight Gains for Normal Cement in Lipid

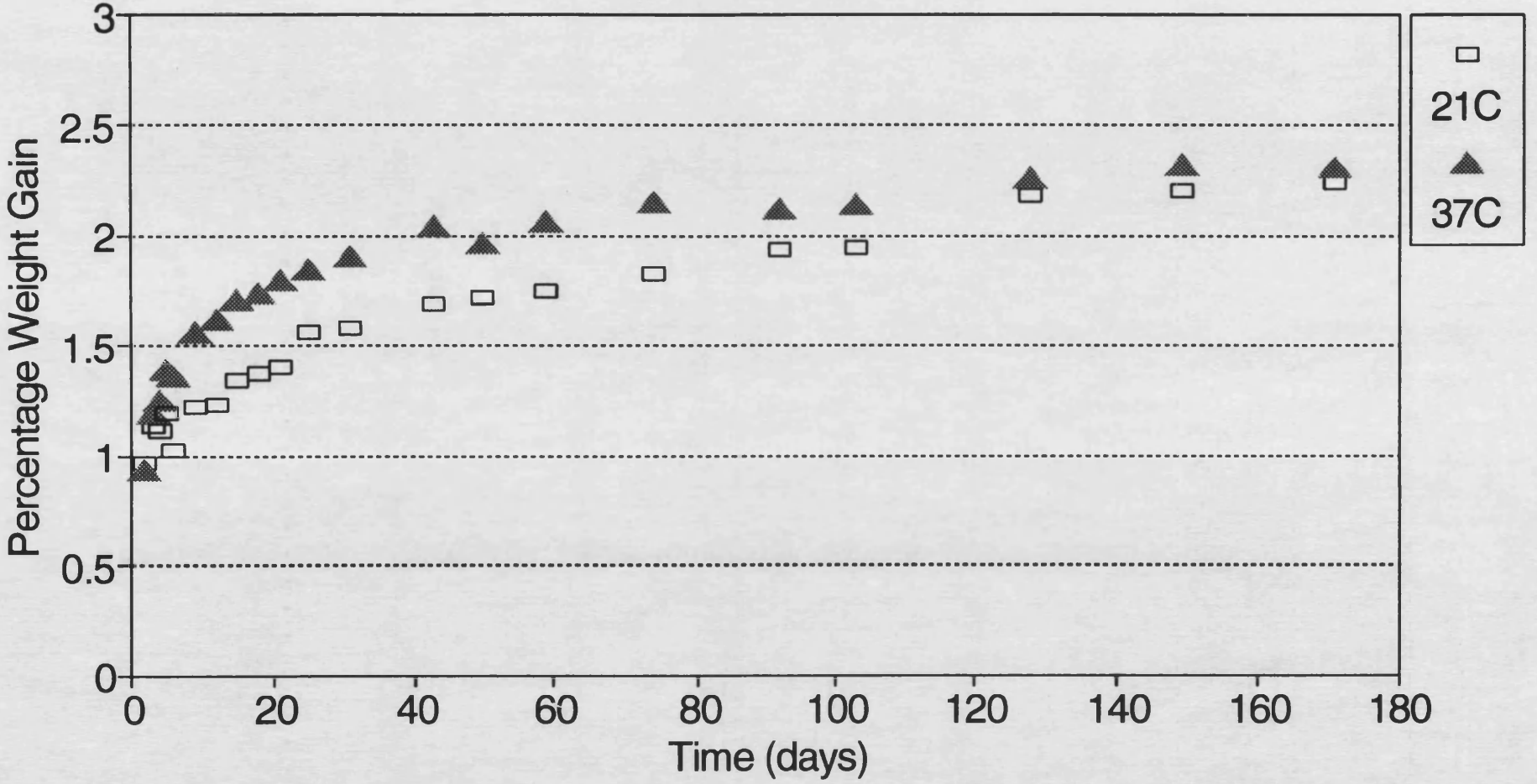


Figure 6.5 : Weight Gains for Normal Cement at 21C

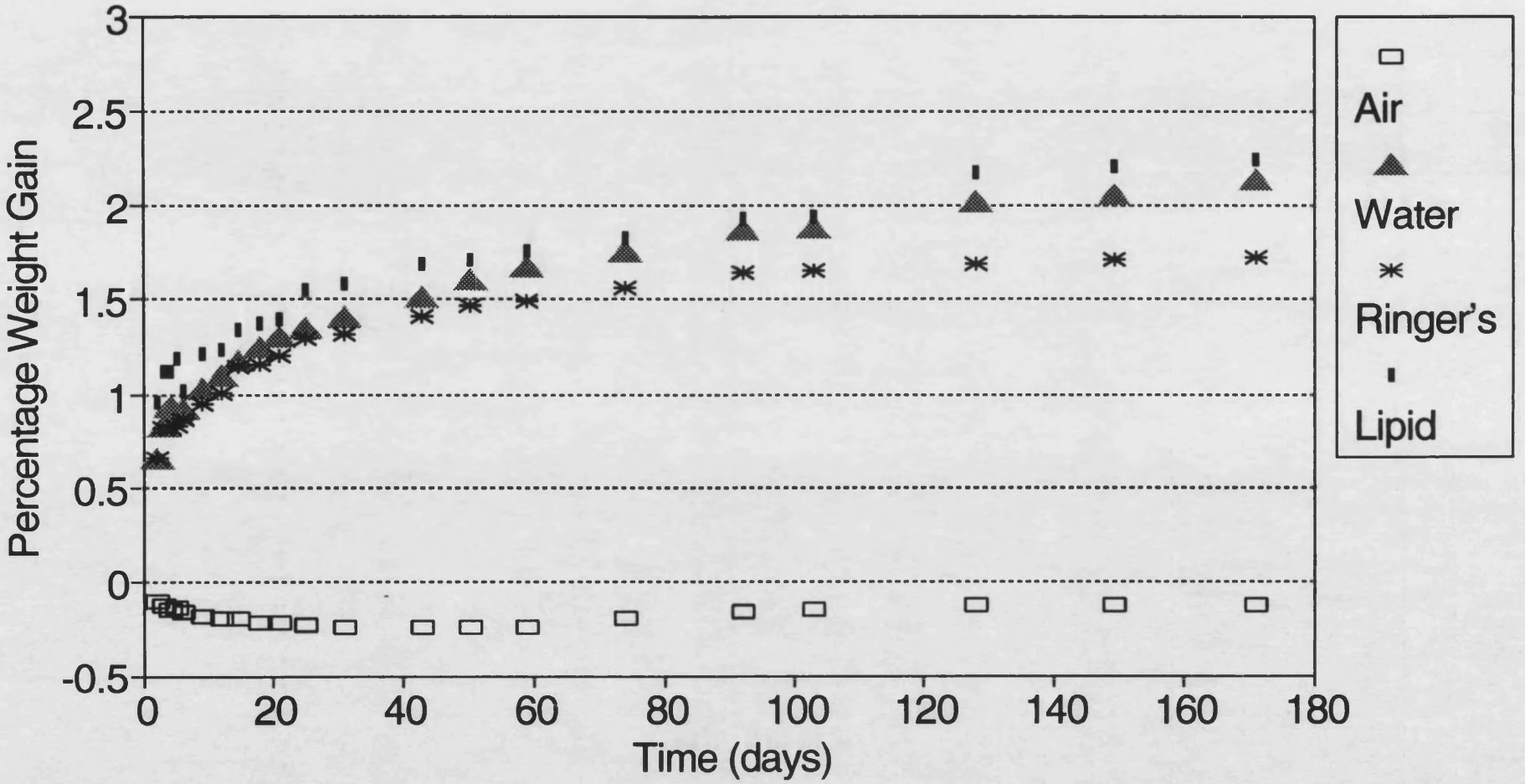


Figure 6.6 : Weight Gains for Normal Cement at 37C

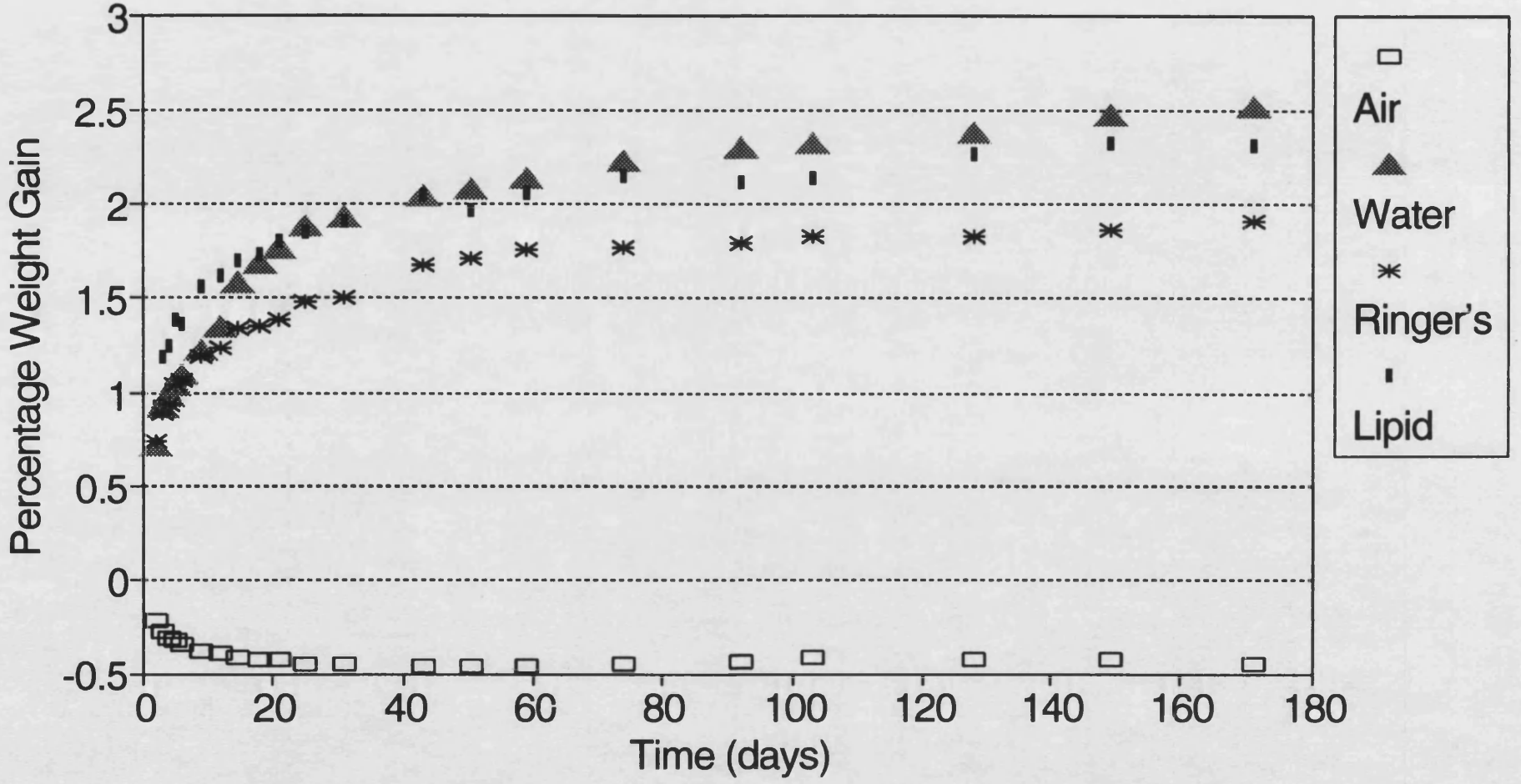


Figure 6.7 : Weight Gains for
Fully Cured Cement in Air

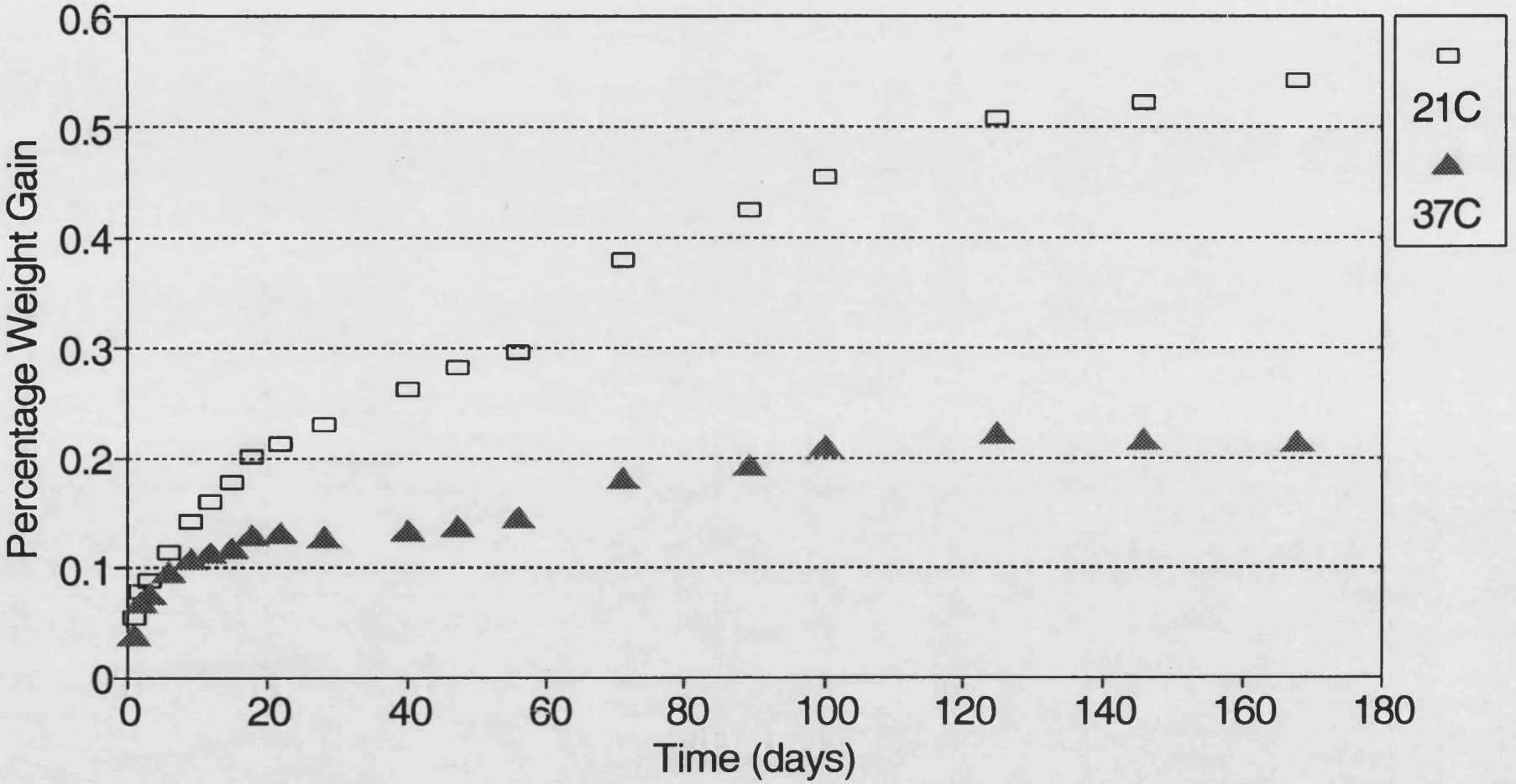


Figure 6.8 : Weight Gains for
Fully Cured Cement in Water

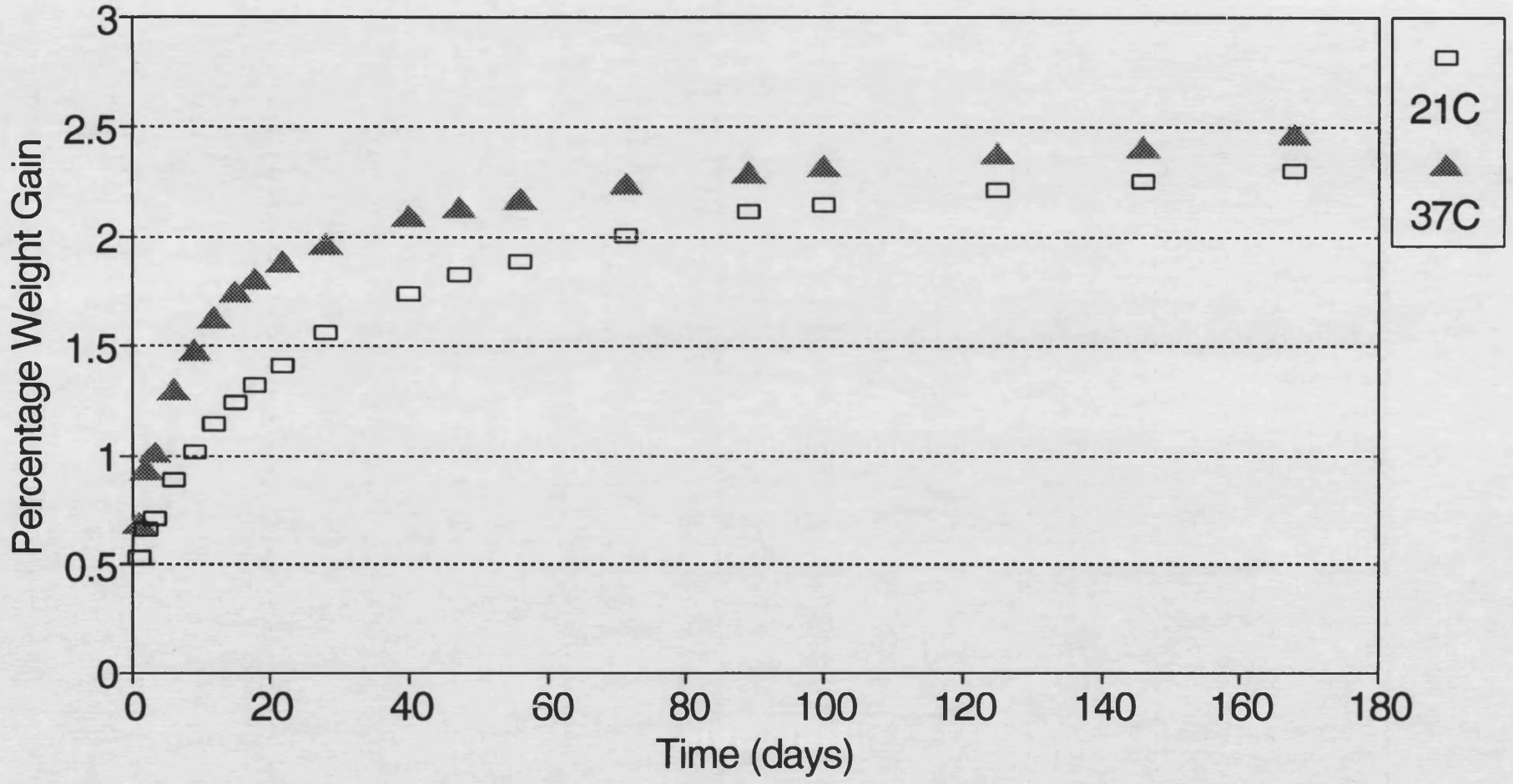


Figure 6.9 : Weight Gains for
Fully Cured Cement in Ringer's

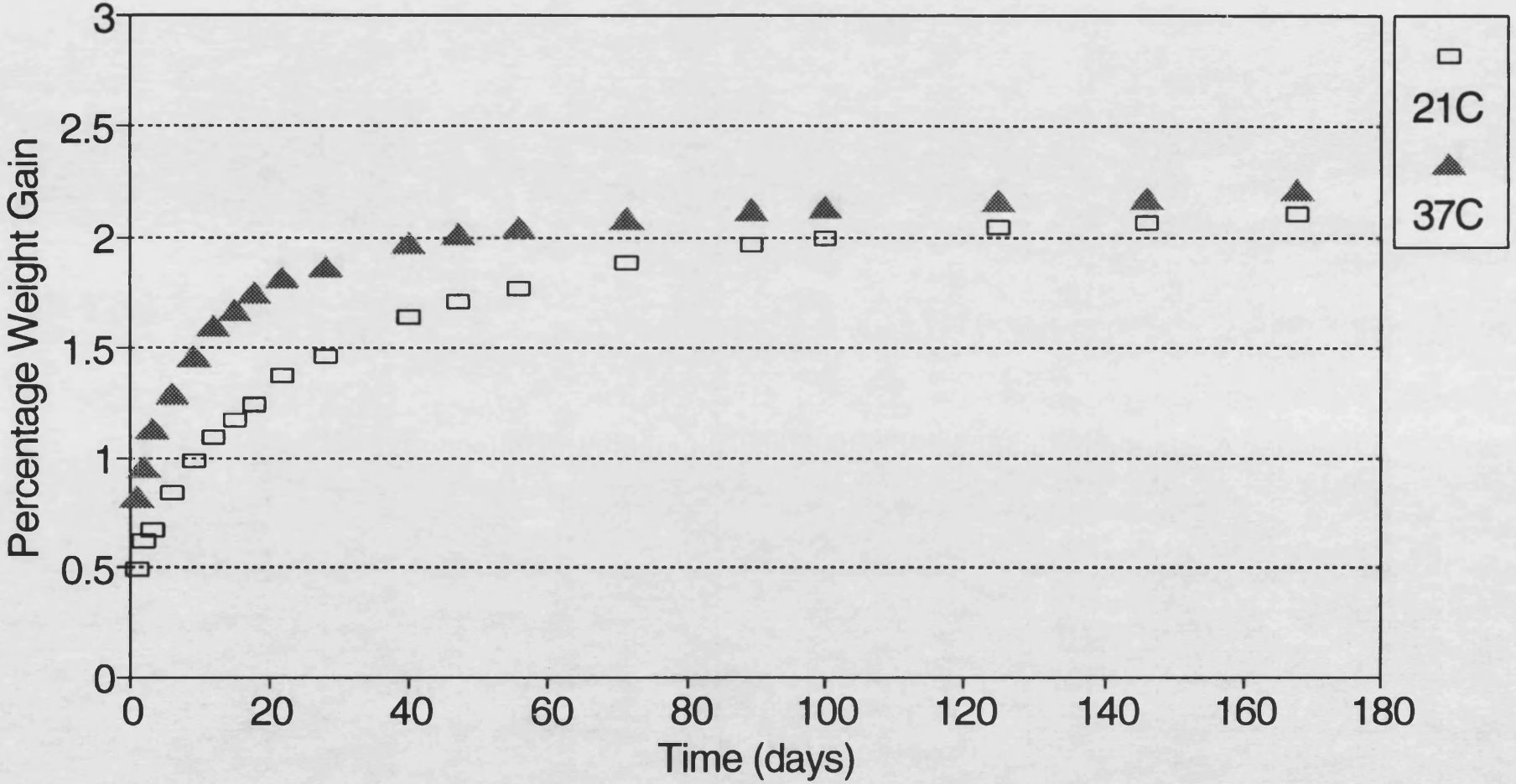


Figure 6.10 : Weight Gains for Fully Cured Cement in Lipid

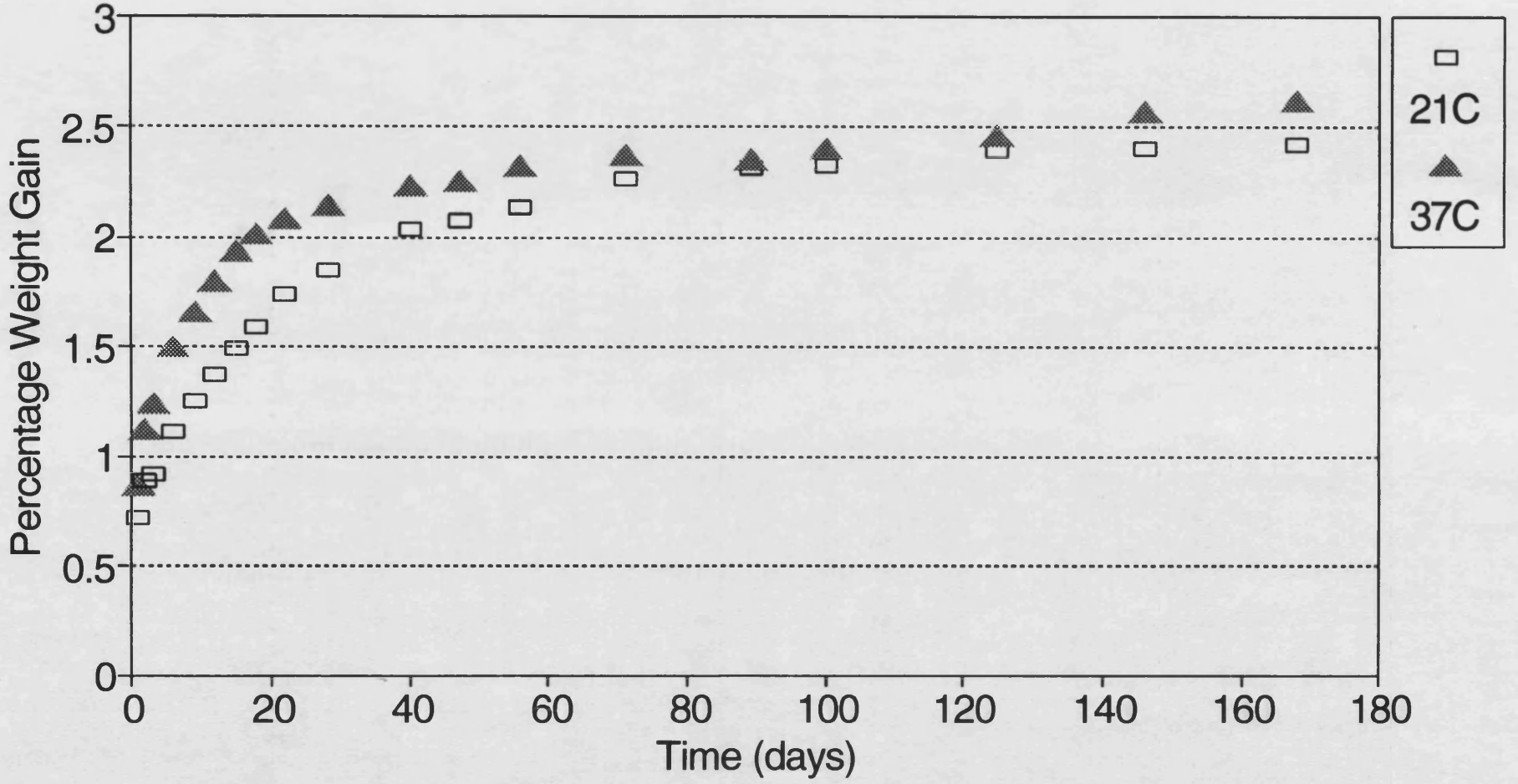


Figure 6.11 : Weight Gains for
Fully Cured Cement at 21C

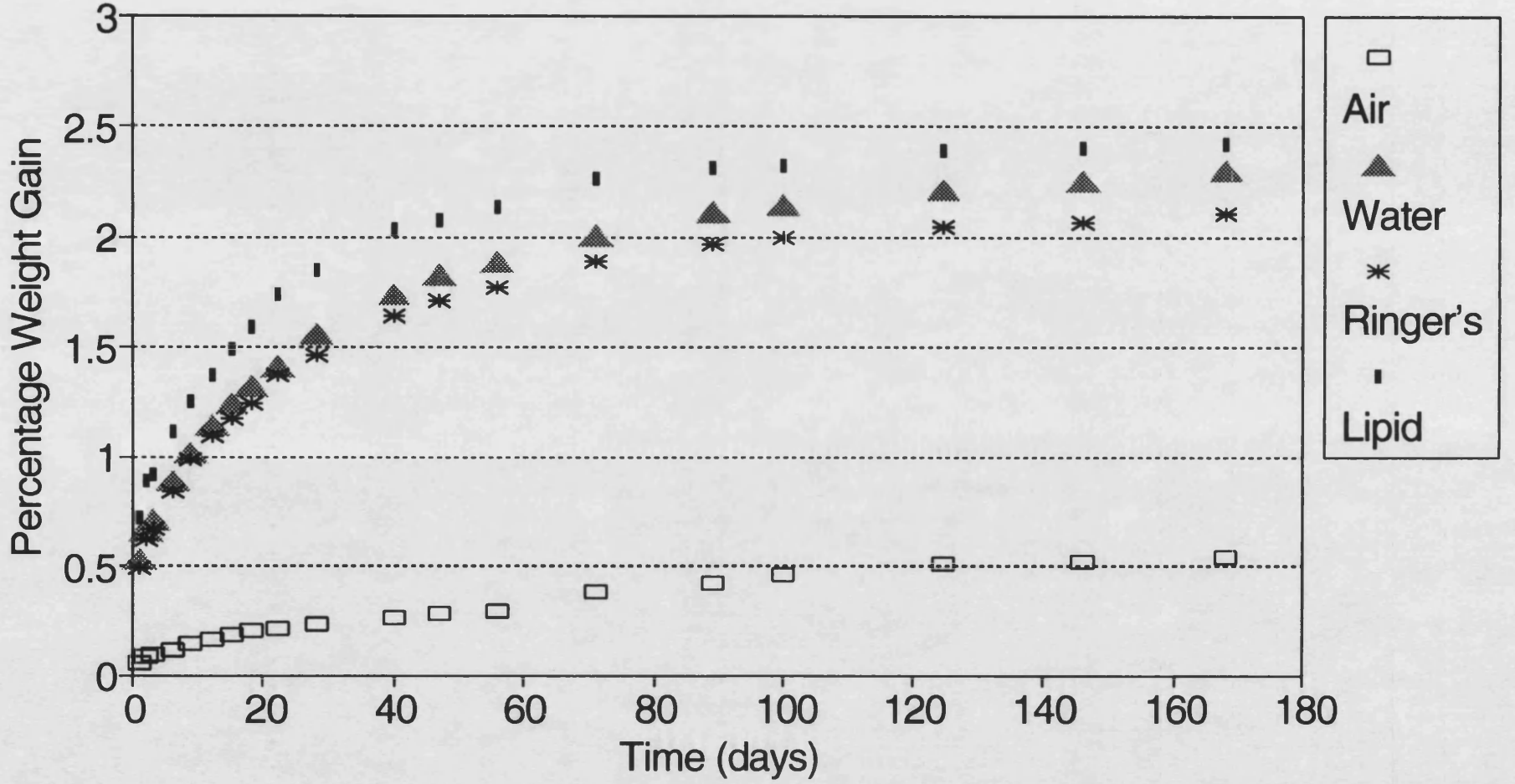
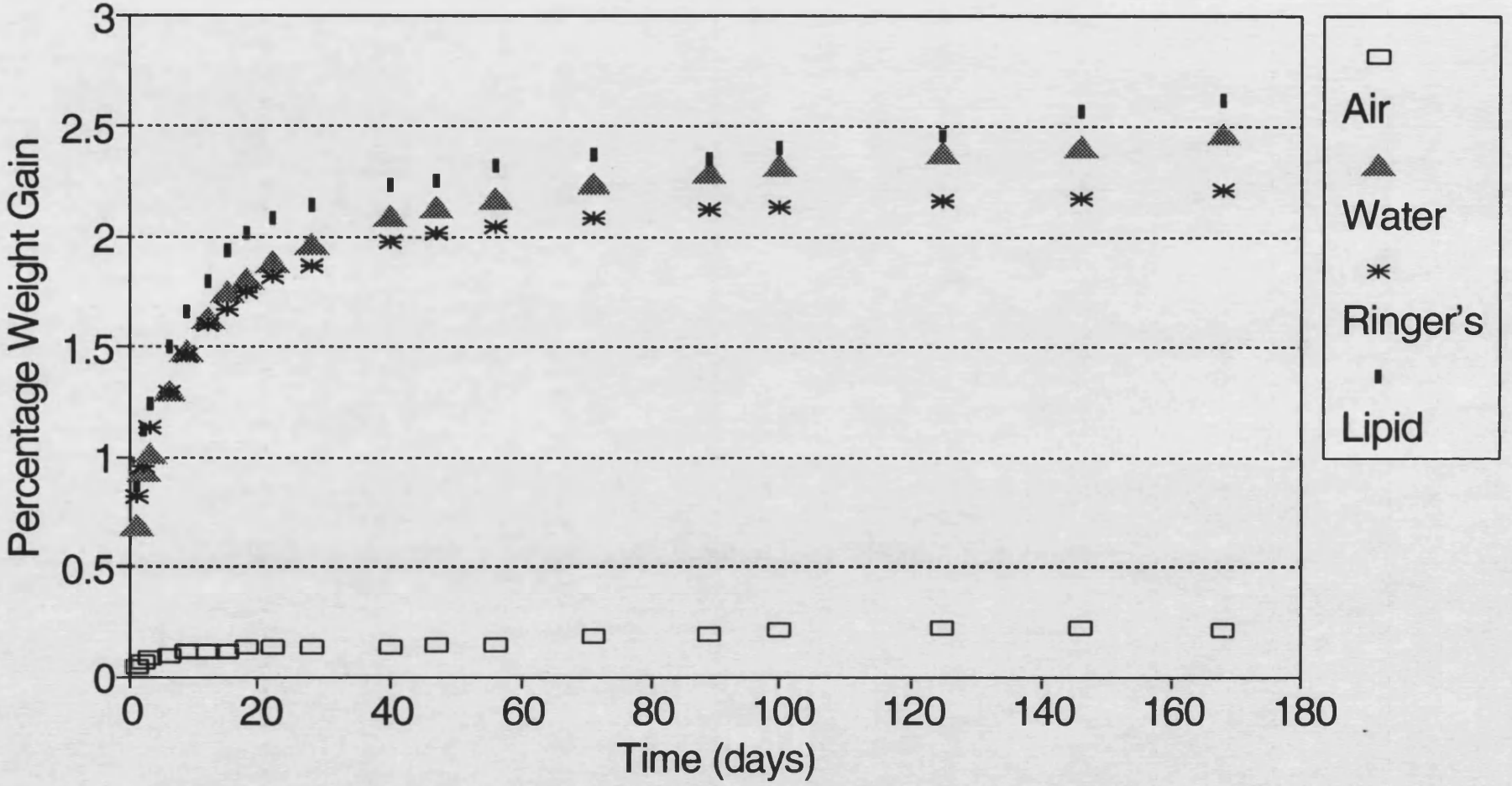


Figure 6.12 : Weight Gains for
Fuly Cured Cement at 37C



7. RESIDUAL MONOMER

7.1 Gas Chromatography Results

7.1.1 Details of the Presentation of the Results

Figure 7.1 shows the gas chromatograph traces for methylmethacrylate monomer, hexane, chlorobenzene, and one of the calibration solutions which contained all three chemicals. Chromatograph traces for cement samples with high and low residual monomer contents are shown in Figures 7.2 and 7.3 respectively.

The gas chromatograph traces for each individual specimen have not been included in this thesis. Instead a summary of the results is presented in tabular form in Tables 7.1 and 7.2. The tables of results give the number of injections, mean residual monomer content (expressed as weight percentage of the mass of the cured cement), standard deviation, and 95% confidence interval (95%CI) for samples stored under several different conditions.

The mean residual monomer contents are also shown graphically in Figures 7.4 - 7.6. Figures 7.4 and 7.5 show the results for samples of normal cement after storage for 3 and 18 months respectively, and Figure 7.6 shows the results for fully cured cement samples after storage for 16 months. The three graphs all show the residual monomer contents superimposed on the WOF results for the particular storage conditions concerned. The symbols on the graphs represent the mean WOF and the mean residual monomer content for the storage condition shown on the x-axis. These conditions are represented by the letters "In", "A", "W", "R", and "L" which correspond to initial, air, water, Ringer's, and lipid respectively, and by the numbers "21" and "37" which correspond to the two storage temperatures. The WOF is plotted on the normal y-axis (on the left hand side), and the residual monomer content is plotted on the second y-axis (on the right hand side). The standard deviations are not shown on the graphs to allow easier comparison of the results, however, the statistical significance of the trends identified in this chapter are presented in Appendix C.

7.1.2 Results for Normal Cement

The gas chromatography results for samples of normal bone cement after storage under various conditions are presented in Table 7.1. These results are also shown graphically, along with the WOF values for the storage conditions concerned, in Figures 7.4 and 7.5.

From Figures 7.4 and 7.5, considering each temperature separately, it can be seen that samples stored in air had a higher residual monomer content than those stored in the three fluid media. Figure 7.5 also shows that there was no apparent difference between the monomer content of samples stored in water and that of those stored in Ringer's. It can be seen that storage of samples in lipid resulted in the lowest residual monomer content of all the storage media. Both graphs show that in all four of the storage media, samples stored at 37°C had a lower residual monomer content than those stored at 21°C.

Comparing Figures 7.4 and 7.5, it can be seen that there was little difference in the residual monomer content of samples stored in air and water for 3 months and those stored in the same environments for 18 months. However, for samples stored in lipid there was a small decrease in the monomer content between those stored for 3 and those stored for 18 months. When the results for both storage periods were compared with the initial residual monomer content (In), it was apparent that in all four media, most of the residual monomer was lost within the first few weeks of storage.

The WOF results for the various storage conditions are also shown in Figures 7.4 and 7.5. It can be seen from these graphs that a lower residual monomer content usually corresponded to a lower WOF value. For example, all the samples had both a lower WOF value and a lower residual monomer content when stored at 37°C as opposed to 21°C. Also samples stored in lipid as opposed to water, had both a lower WOF value and a lower residual monomer content.

7.1.3 Results for Fully Cured Cement

The gas chromatography results for the fully cured cement samples are given in Table 7.2, and are shown graphically, along with the WOF results, in Figure 7.6.

Comparing Figures 7.5 and 7.6, it can be seen that the residual monomer content of the fully cured cement was much lower than that of the normal cement. Figure 7.6 also shows that the monomer content was not influenced by the various storage conditions. After 16 months storage, samples from each of the eight different storage environments had very similar residual monomer contents. There were also no differences between the initial monomer content and those after 16 months storage in the various environments.

Since the storage environments did not influence the monomer content of the fully cured cement, there was no apparent relationship between WOF value and residual monomer content. In other words, although there were dramatic differences between the WOF results for the various storage environments, there was no variation in the monomer contents for these same environments.

7.2 Discussion of Gas Chromatography

7.2.1 Normal Cement

Care must be taken when comparing the individual residual monomer contents evaluated in this thesis to those of others authors, as although considerable work has been done on the leaching of methylmethacrylate monomer from acrylic dental resins, dental resins generally contain considerably more residual monomer than bone cements (Brauer, Termini and Dickson, 1977). This is because the chemically activated dental acrylics tend to be cross linked which slows the diffusion of the

monomer and chain radicals within the resin (Lautenschlager, Stupp and Keller, 1984). For example, in a study of three different dental resins Scheerer, Swartz, Norman and Phillips (1964) reported residual monomer levels ranging from 6.5% to 11.1% after storage of samples in air for 1 hour. So the actual values of residual monomer content obtained with dental resins can not be directly compared with those obtained for bone cement in this thesis, it is only valid to compare the trends observed with dental resins with those observed with bone cements.

7.2.1.1 Initial Monomer Levels

Various levels for the residual monomer content of cured bone cement have been suggested in the literature. Gilding and Emery (1977) reported residual monomer levels of 25-30% at dough time, 12-17% at the exotherm peak, and 6-8% at setting time, although the authors did not specify the brand of cement tested. Haas, Brauer and Dickson (1975), and Brauer, Termini and Dickson (1977) reported a 3.3% residual monomer content after storage of Simplex P radiolucent specimens in air at room temperature for between 30 and 60 minutes. In this thesis a residual monomer content of 2.2% was measured for radiopaque Simplex P bone cement tested 30 minutes after curing. When the weight of the barium sulphate was taken into account (the weight of barium sulphate is approximately 6.8% of the cured cement, (Brauer, Termini and Dickson, 1977)), a value of 2.4% residual monomer was obtained, based solely on the resin content. This was significantly lower than the values reported above, and was probably due to differences in the techniques for mixing and curing the samples, which Gilding and Emery (1977) suggested could lead to "considerable variation in the amount of monomer in different samples".

Haas, Brauer and Dickson (1975), and Brauer, Termini and Dickson (1977) also reported values for the residual monomer content of 2.7% and 2.4% for samples stored in air at room temperature for 20 hours and 215 days respectively. In this thesis little difference was found between the monomer content after 84 days and that after 553

days for samples stored in air at 21°C, the value for both being approximately 1.6%. This value was again for the radiopaque cement, which when based solely on the resin content becomes 1.7%, which is again significantly lower than the values reported by Brauer *et al* (1977), but could still be due to differences in the mixing techniques between the two groups of workers. In this study if the residual monomer contents of the two samples which were mixed independently, from different batches of cement, and on different days, but were stored under the same conditions are compared - the two samples stored in air at 21°C for 84 days (see Table 7.1) - then within experimental error the two monomer contents were found to be almost identical (1.58% and 1.59%). So the variation between the monomer contents of samples prepared in the same laboratory, under the same conditions was negligible, and the testing of only one sample per storage environment can be justified. This is especially true as in this thesis the main aim of this section was to identify trends in the residual monomer content of the cement after storage under different conditions, rather than to evaluate the specific monomer content for a particular sample. Also, all the samples in each of the time periods studied were mixed on the same day, under the same conditions, thus the problem of any slight variations in the residual monomer content due to slightly different ambient conditions was eliminated.

In a study to monitor the rate of polymerisation of three different dental resins by measuring their respective residual monomer contents, Scheerer, Swartz, Norman and Phillips (1964) reported monomer levels ranging from 8.9% to 32.2% for the different resins 5 minutes after mixing was started. The authors found that 60 minutes after mixing these values had fallen to between 6.5% and 11.1%, and to between 5.3% and 7.5% after storage in air at room temperature for 6 weeks. Despite the slightly higher residual monomer contents of the dental resins tested in the study by Scheerer *et al* (1964) (and the differences between the three types of resin), the effect of their storage in air at room temperature was very similar to that observed in this thesis. After the bone cement had polymerised there was little change in the monomer content with

storage in air, only a slight decrease with storage time. In two of the dental resins studied Sheerer *et al* (1964) found decreases in monomer content of approximately 0.7% between storage for 1 hour and that for 6 weeks in air at room temperature. The monomer content of samples of bone cement used in this thesis, tested 30 minutes after curing (45 minutes after mixing) had decreased by 0.6% when similar samples were tested after storage for 12 weeks in air at 21°C. There was then no further decrease in the monomer content of samples tested after 18 months of storage. The values obtained in this thesis are therefore consistent with the previous studies which are discussed above.

7.2.1.2 Effect of Storage Environment

As discussed in section 7.1.2 the residual monomer content was highest for the sample tested immediately (2 hours) after curing, followed closely by the samples stored in air. Storage of samples in lipid resulted in the lowest residual monomer content of all the media, with the monomer contents of samples stored in water and Ringer's falling between the values for air and lipid. There was no difference between the monomer contents of samples stored in water and those stored in Ringer's. This implied that the monomer, which is known to be a powerful lipid solvent (Howmedica, 1989), leaches easily into the lipid medium, but leaches less readily into air and the two water based media. Therefore it is not surprising that the monomer had a greater affinity for the lipid medium than it did for water, hence allowing more monomer leach from the cement when it was stored lipid as opposed to water or Ringer's. The samples which were stored in lipid had an initial residual monomer content of 2.2%, and within 3 months of storage at 37°C this had decreased to value of approximately 0.2%. This suggests that virtually all the residual monomer in cured cement could be leached out into the fat within the joint cavity by a few months after insertion.

It has been shown by various workers (see section 2.5) that methylmethacrylate monomer can be detected in the blood of patients undergoing joint replacement

operations. Albrektsson (1985) and Willert, Frech and Bechtel (1975) have shown that the residual monomer has the greatest affinity for tissues which are rich in fat cells, due to the fat solubility of the monomer. The leaching of monomer into the fatty tissues may have an associated toxic effect on the tissue, and could also have the same effect on the fracture behaviour of the cement as the leaching of monomer which has been observed in this thesis.

As discussed above, samples which were stored in water lost more residual monomer than those which were stored in air. This is consistent with the work of Basker, Collier, Smith, Bartle, Frere and Wong (1989) who suggested that this was not due to the leaching of the monomer into the water, but instead due to the continued curing of the water stored cement (as discussed in section 2.5).

In this thesis the residual monomer contents of radiopaque bone cement samples which were stored in water at 37°C for 3 and 18 months were virtually the same, with an approximate value of 0.5%. This was significantly lower than the value obtained by Brauer, Termini and Dickson (1977) of 1.4% after storage in water at 37°C for 4.5 months. When the correction for the barium sulphate was made a value of 0.6% was obtained, based solely on the resin content of the cement. The variation in these results has been attributed to differences in the mixing and storage techniques, as discussed previously.

Although the storage water was not saturated with monomer (see Appendix B), only a small portion of the residual monomer leached into the water, and this was achieved in a relatively short period of time, with no changes for longer storage periods. Since the glass storage jars were regularly shaken, it is unlikely that any monomer accumulated locally in the water immediately next to the samples, causing local saturation of the water. Also since the monomer continued to leach from the cement which was stored in lipid after storage for 3 months, it is unlike that internal migration of the monomer

through the bulk of the cement was responsible for the residual monomer contents of the water stored samples being significantly higher than those stored in lipid. Interestingly, Linder, Harthon and Kullberg (1976) also found similar results, that the leakage of monomer from cement samples was much lower than had been expected. The authors were also unable to explain this finding. Since this thesis was concerned with measuring the monomer content of the cement samples themselves, continued curing of the cement can not be offered as an explanation of these results. One possible explanation is that the diffusion of monomer out the cement will be time dependant, and as the solubility of monomer in water is much lower than that in lipid the plateau region where the diffusion becomes extremely slow will be reached more quickly with water than with lipid. This would explain the difference between the monomer levels at 3 and 18 months after storage in lipid, but why there was no difference between the two time periods in water. Linder, Harthon and Kullberg (1976) suggested that the medium in which the cement was stored would not be important so long as the monomer was removed from the surface of the cement more rapidly than the rate of diffusion of monomer through the cement mass. This thesis does not support this view, as samples which were stored in lipid were found to have a much lower residual monomer content than samples which had been stored in water.

The literature suggests that there is a portion of the residual monomer which is water soluble and a portion which is not. This could explain why only a small percentage of the residual monomer leached into the storage water used in this study, when it has been shown in Appendix B that the water had not become saturated with monomer. It was suggested by Smith and Bains (1956) that the non water soluble monomer was trapped within the cement structure. If this was the case then it is unlikely that the change to a lipid storage medium would have allowed this portion of the monomer leach out as our results suggest it does.

7.2.1.3 Effect of Storage Period

Section 7.1.2 also showed that there was no difference between the monomer contents of samples stored for 3 months and those stored for 18 months in both air and water. However, for samples stored in lipid the monomer content after storage for 18 months was less than that after 3 months. These results showed that in air and water, the monomer leached out of cement over the first few weeks, with no further leaching after that period. In lipid the monomer was still continuing to leach out from the cement after storage for over 3 months. This observation supports that discussed above, that more monomer leaches into lipid than into air or water.

7.2.1.4 Effect of Storage Temperature

The results given in section 7.1.2 also showed that in all four of the storage media, samples which were stored at 37°C had a lower residual monomer content than those stored at 21°C. Although the solubility of methylmethacrylate in water decreased slightly with an increase temperature, it is very unlikely that it would have decreased below the saturation point. Thus the only effect of storage at the higher temperature would have been to increase the diffusion and mobility of the monomer, which in turn would have either allowed continued curing of the cement, or made it easier for the monomer to leach into the storage media. Unfortunately in this thesis only the residual monomer content of the cement was measured, and the amount of monomer which had leached into the storage media was not monitored. There have been no other studies which have examined the effect of storage temperature on the leaching of monomer from acrylic cement. Therefore it is uncertain as to whether continued curing occurred or whether the lower monomer content was due to increased leaching of the monomer into the storage media.

Linder, Harthon and Kullberg (1976) suggested that the leaching of residual monomer from bone cement would be unaffected by storage at different temperatures after mixing had ceased. The authors cited Bayne (1974) in support of this statement.

Linder *et al* (1976) suggested that the results which they obtained for the leaching of monomer from cement in water at 20°C would have been the same if the experiment had been conducted in a water bath at 37°C. In this thesis it was found that storage of samples at the higher temperature lead to a significantly greater loss of monomer than did storage at 21°C. In a study by Bayne, Lautenschlager, Greener and Meyer (1977) it was shown that the temperature during mixing controlled the setting time of the cement without significantly affecting the rate nor the quantity of monomer released. This would suggest that the decrease in residual monomer content observed in this thesis was due to continued curing of the cement at the higher temperature rather than increased leaching of the monomer. Linder *et al* (1976) also suggested that a higher rate of leaching of monomer into blood as opposed to water would not be expected as the monomer solubility in blood would be similar to that in water. This is probably correct, but the bone cement is not just interfacing with blood, there is also a very high fat content in the bone cavity into which the cement is inserted. The results of this thesis suggest that monomer will leach more readily into a lipid rich medium than a water based one, and hence that there would be a difference between the amount of monomer leached out *in vivo* and that reported in the laboratory studies mentioned here.

7.2.1.5 Evaluation of the Test Technique

In this thesis only the amount of monomer which leached into the various environments after the cement had cured in air at 21°C for 30 minutes was evaluated. One would expect significantly more monomer to leach out in vivo since the cement is also cured whilst in contact with the physiological fluids. Attempts have been made to evaluate the monomer release from bone cement during simulated in vivo curing (Schoenfeld, Conard and Lautenschlager, 1979, Brauer, Termini and Dickson, 1977, and Linder, Harthon and Kullberg, 1976). Comparing the amount of monomer leached out into the aqueous solution in the study by Schoenfeld *et al* (1979), to that measured in this thesis, it was found that considerably less monomer was lost in the latter,

0.005g over 3 months in this thesis compared to 0.05g over 1 hour in the study by Schoenfeld *et al* (1979). The values of monomer lost from the cement obtained from this thesis were measured indirectly as changes in the monomer content of the cement with time, and not as actual measurements of the amount of monomer leached out, therefore some of the monomer lost in this thesis may have been lost due to continued curing rather than due to leaching into the storage media.

Although using our method for evaluating the monomer release from bone cement does not distinguish between monomer leached into the surrounding media and that lost due to continued curing, at least a definite measure of the monomer content of the cement with time of storage was obtained. Problems have been reported with the techniques which measure the amount of monomer in the media surrounding the cement (Linder, Harthon and Kullberg, 1976, and Brauer, Termini and Dickson, 1977). Both groups found that as the release of monomer began to stabilise after the cement had set, the monomer concentration in the surrounding media began to unexpectedly decrease instead of remaining steady. The latter group attributed the decrease in monomer concentration to either the polymer or the test equipment absorbing the monomer, whereas Linder *et al* (1976) attributed the decrease in monomer concentration to the monomer evaporating from the water storage medium.

7.2.2 Fully Cured Cement

The gas chromatography results given in section 7.1.3 showed that the residual monomer content of the fully cured cement was significantly lower than that of the normal cement. Hence the method suggested by Beverley (1990) for virtually eliminating the residual monomer from the cement was successful. The dependence of the residual monomer content of dental acrylics upon the curing cycle of the resin has also been reported elsewhere (Huggett, Bates and Packham, 1987, and Smith and Bains, 1956). It was found by Smith and Bains (1956) that dental acrylics which were

cured at room temperature had a higher residual monomer content than those which had been cured by boiling.

Smith (1961) has shown that the residual monomer content of dental acrylics can be reduced to 0.2-0.3% (a level which the author described as minimal) by heat treatment of the polymer. This value for a minimum level of residual monomer in a heat treated acrylic resin compares well the values obtained in this study on fully cured bone cement (see in Table 7.2).

It was also shown in section 7.1.3 that there were no differences between the sample tested immediately (2 hours) after heat treatment and those stored in the various environments for 16 months. There were also no differences between samples stored in air, those stored in water, nor those in lipid. Neither were there any differences between samples stored at the two different temperatures. It was expected that at least in the lipid medium the monomer levels would decrease to at least the same values as for the normal material stored under the same conditions. The fact the fully cured samples which were stored in lipid for 16 months had a higher residual monomer content than samples of normal cement stored in lipid for 3 months, and that the monomer contents of the fully cured immediate sample and the fully cured samples stored in lipid were very similar, implied that the residual monomer had become trapped within the fully cured cement possibly due to the heat treatment process.

No other work has been published on fully cured, or heat treated, bone cement, so there is no available literature to refer to for possible explanations for the higher than expected residual monomer content of the fully cured material. Three possible explanations are, however, tentatively discussed below.

It is postulated here that maintaining the cement above the glass transition temperature (T_g) for 15 hours may not only have increased the mobility of the monomer units

allowing them to tag onto the ends of existing chains, but may also have increased the mobility of the polymer chains themselves. This could have led to a reorganisation of the chains into a more ordered arrangement, which had the effect of trapping the monomer units within the polymer network. An alternative hypothesis is that the heat treatment may have induced cross-linking into the polymer network of the fully cured cement, thus removing possible pathways for diffusion of the monomer out of the cement mass.

A final possible explanation for the persistence of approximately 0.2% residual monomer in the fully cured cement is that the powder component of the radiopaque cement contains approximately 0.25% methylmethacrylate monomer, which equates to approximately 0.2-0.3% by weight of the cured sample (Brauer, Termini and Dickson, 1977). If this residual monomer is unextractable, then the residual monomer content of the powder component would account for the measured monomer content of the fully cured samples, and the differences between the monomer contents of the normal and the fully cured cement could be due to experimental error.

7.3 Comparison of the Reductions in Residual Monomer Content and the Actual Weight Losses for Samples Stored in Air

The weight of monomer lost as estimated from the gas chromatography results (given in section 7.1.2), can be easily compared with the actual weight loss results from the environmental ingress results (given in section 6.1.2) for normal cement stored in air. The residual monomer content of samples tested immediately (30 minutes) after curing was found to be 2.2%, which corresponds to a weight of approximately 0.0062 ± 0.0002g of methylmethacrylate. Samples which had been stored in air at 21°C for 84

days had a residual monomer content of 1.6%, which was equivalent to approximately 0.0045 ± 0.0002g of methylmethacrylate. Thus after storage in air at 21°C for 84 days, the samples of bone cement had lost approximately 0.0017 ± 0.0005g of monomer as estimated from the gas chromatography results. However, some of this monomer may have been lost due to continued curing rather than due to evaporation from the surface of the cement, so this estimation of expected weight loss is probably a little high.

From the environmental ingress results it was shown that specimens stored in air at 21°C for 74 days lost an average of 0.19 ± 0.03% in weight, which corresponds to approximately 0.003 ± 0.001g. Repeating the procedure for specimens stored at 37°C gave weight losses of the monomer of 0.0043 ± 0.0005g, estimated from the gas chromatography results, and 0.007 ± 0.001g, calculated from the environmental ingress results. Hence it can be seen that for specimens stored at both temperatures the actual weight losses were approximately twice those estimated from the gas chromatography results. However, once experimental error had been taken in account, the two values of weight loss were not dissimilar. As the gas chromatography results are likely to give a higher estimated monomer loss than that due solely to evaporation of the monomer, it would appear that when specimens are stored in air it is not just monomer which is lost from the cement. Other volatile substances such as residual initiator, accelerator, or stabiliser must also be evaporated from within the cement mass.

The cement when first set was found to contain 2.2% residual monomer (from the gas chromatography results) which corresponds to 0.05g of methylmethacrylate in each of the environmental ingress specimens. Hence there was 0.05g of monomer available to evaporate from within the cement mass. The weight losses after 171 days in air at 21°C and 37°C were 0.12% (0.002g) and 0.45% (0.007g) respectively. Therefore only a small percentage (approximately 4% at 21°C and 14% at 37°C) of the residual monomer did evaporate from the cement during storage in air. Since the gas

chromatography estimation of the weight loss was less than the actual weight loss, it is unlikely that much of the residual monomer was lost due to continued curing. Therefore approximately 1.6% residual monomer will remain within the polymer network of the normal cement which is stored air.

7.4 Summary of Gas Chromatography

It was found that bone cement contains residual monomer which leaches out from the cement with time, and that this leaching is strongly influenced by both the storage medium and the storage temperature. Higher storage temperatures led to increased leaching of the monomer, as did a lipid storage medium compared to water or air.

It has been shown that the WOF of bone cement was closely related to its residual monomer content. A high residual monomer content corresponded to a high WOF, due to the plasticising effect of the monomer. Therefore it would be desirable to minimise the leaching of the monomer *in vivo*.

There have been no other studies which have monitored the leaching of residual monomer from bone cement into fat solutions, which is surprising as it is well known that the monomer is a powerful lipid solvent, and that there is a very high fat content in the bone marrow of the joint cavity into which the cement is inserted. A probable reason for this lack of research into storage of bone cements in lipids is because the initial work on leaching of residual monomer from bone cements was based on work done on dental resins where the problem of monomer leakage into fat was not a concern. However, it has been shown in this thesis and by other workers, that the residual monomer in bone cement does leach into storage media *in vitro*, and into blood and bone tissue *in vivo*. This will have both a toxic effect on the bone tissue

surrounding the cement, and a detrimental effect on the fracture resistance of the cement.

Table 7.1 : Gas Chromatography Results for Normal Bone Cement Samples

Storage Condition	No. of Injections	Mean Residual Monomer Content (%)	Standard Deviation	95% C.I.
Initial	4	2.20	0.07	2.20±0.11
84D-A21°C a	3	1.58	0.01	1.58±0.02
84D-A21°C b	5	1.57	0.13	1.57±0.16
84D-A37°C	5	0.78	0.09	0.78±0.11
84D-W21°C	5	0.95	0.11	0.95±0.14
84D-W37°C	5	0.53	0.08	0.53±0.10
84D-L21°C	7	0.65	0.17	0.65±0.16
84D-L37°C	7	0.24	0.13	0.24±0.12
553D-A21°C	3	1.59	0.02	1.59±0.05
553D-A37°C	4	0.74	0.04	0.74±0.06
553D-W21°C	3	0.95	0.02	0.95±0.05
553D-W37°C	5	0.45	0.14	0.45±0.17
553D-R21°C	5	1.04	0.02	1.04±0.02
553D-R37°C	5	0.42	0.13	0.42±0.16
553D-L21°C	3	0.33	0.02	0.33±0.05
553D-L37°C	5	0.12	0.01	0.12±0.02

NOTES

i) Initial corresponds to samples 30 minutes after curing.

ii) a and b correspond to two different samples.

iii) 84D corresponds to 84 days (3 months).

iv) 553D corresponds to 553 days (18 months).

v) A21°C corresponds to air at 21°C. W, R, and L correspond to water, Ringer's, and lipid respectively.

Table 7.2 : Gas Chromatography Results for Fully Cured Bone Cement Samples

Storage Condition	No. of Injections	Mean Residual Monomer Content (%)	Standard Deviation	95% C.I.
Initial	6	0.24	0.11	0.24±0.12
84D-A21°C	5	0.32	0.11	0.32±0.14
455D-A21°C	4	0.31	0.01	0.31±0.02
455D-A37°C	20	0.40	0.17	0.40±0.08
455D-W21°C	6	0.30	0.08	0.30±0.08
455D-W37°C	7	0.16	0.04	0.16±0.04
455D-R21°C	7	0.33	0.18	0.33±0.17
455D-R37°C	4	0.23	0.08	0.23±0.13
455D-L21°C	5	0.30	0.05	0.30±0.06
455D-L37°C	12	0.32	0.13	0.32±0.08

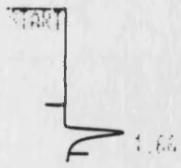
NOTES

i) Initial corresponds to samples 30 minutes after heat treatment.

ii) 84D corresponds to 84 days (3 months).

iii) 455D corresponds to 455 days (15 months).

iv) A21°C corresponds to air at 21°C. W, R, and L correspond to water, Ringer's, and lipid respectively.



STOP

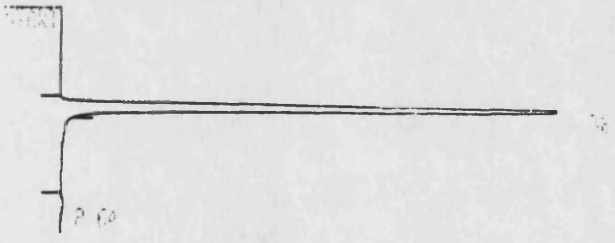
RUN # 26

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.66	47124	PB	0.114	100.000

TOTAL AREA= 47124
MUL FACTOR= 1.0000E+00

Figure 7.1a : Gas Chromatography Trace for Methylmethacrylate Monomer.



STOP

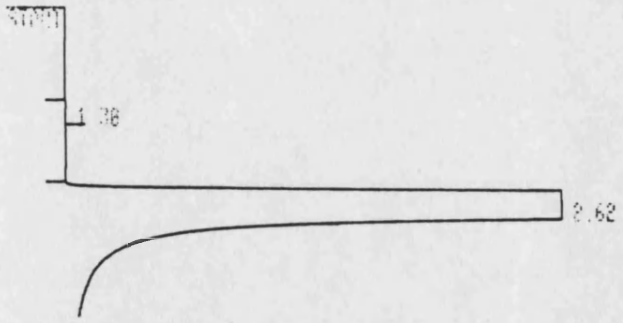
RUN # 25

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.32	391400	PB	0.080	98.722
2.64	5067	I PP	0.102	1.278

TOTAL AREA= 396468
MUL FACTOR= 1.0000E+00

Figure 7.1b : Gas Chromatography Trace for Hexane.



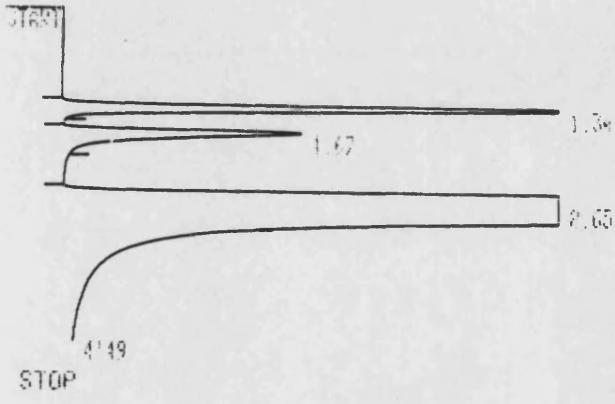
RUN # 2?

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.30	1112	PD	0.094	0.004
2.62	2.7533E+07	PB	0.175	99.996

TOTAL AREA= 2.7535E+07
MUL FACTOR= 1.0000E+00

Figure 7.1c : Gas Chromatography Trace for Chlorobenzene.



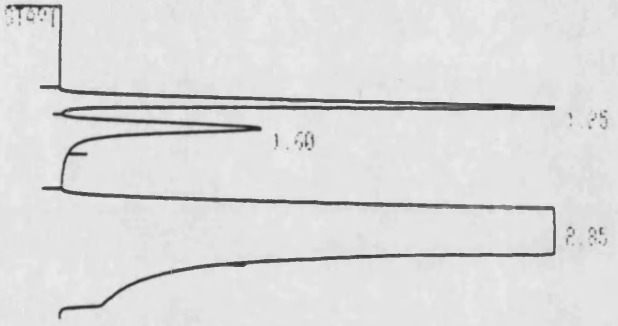
RUN # 2?

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.34	33970	PB	0.080	1.221
1.67	221190	PB	0.126	0.799
2.65	2.7126E+07	PB	0.172	97.980

TOTAL AREA= 2.7685E+07
MUL FACTOR= 1.0000E+00

Figure 7.1d : Gas Chromatography Trace for one of the Calibration Solutions.



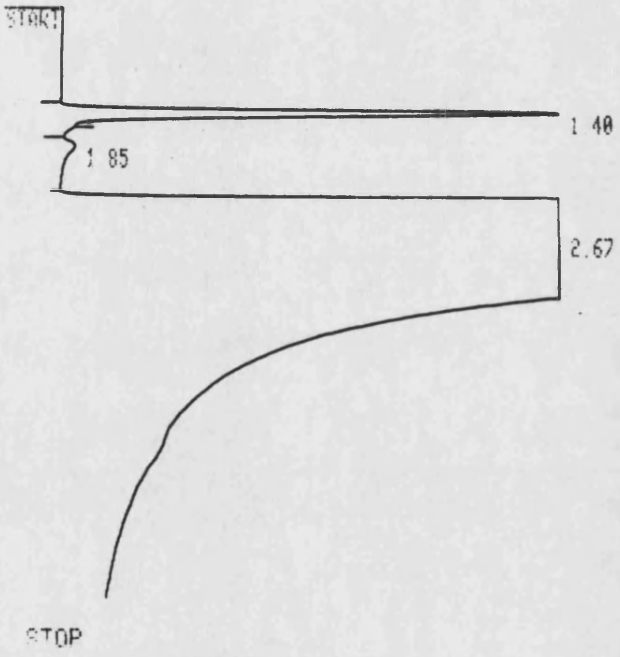
RUN # 22

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.25	396000	PP	0.103	1.470
1.60	245200	PB	0.166	0.910
2.85	2.6306E+07	PB	0.284	97.621

TOTAL AREA= 2.6942E+07
MUL FACTOR= 1.0000E+00

Figure 7.2 : Gas Chromatography Trace for a Cement Sample with a High Residual Monomer Content.



RUN # 61

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.40	356300	PB	0.096	0.135
1.85	19436	BP	0.218	0.007
2.67	2.6398E+08	*SPH	0.538	99.858

TOTAL AREA= 2.6436E+08
MUL FACTOR= 1.0000E+00

Figure 7.3 : Gas Chromatography Trace for a Cement Sample with a Low Residual Monomer Content.

Figure 7.4 : WOF versus GC Results
for Normal Cement after 3 Months

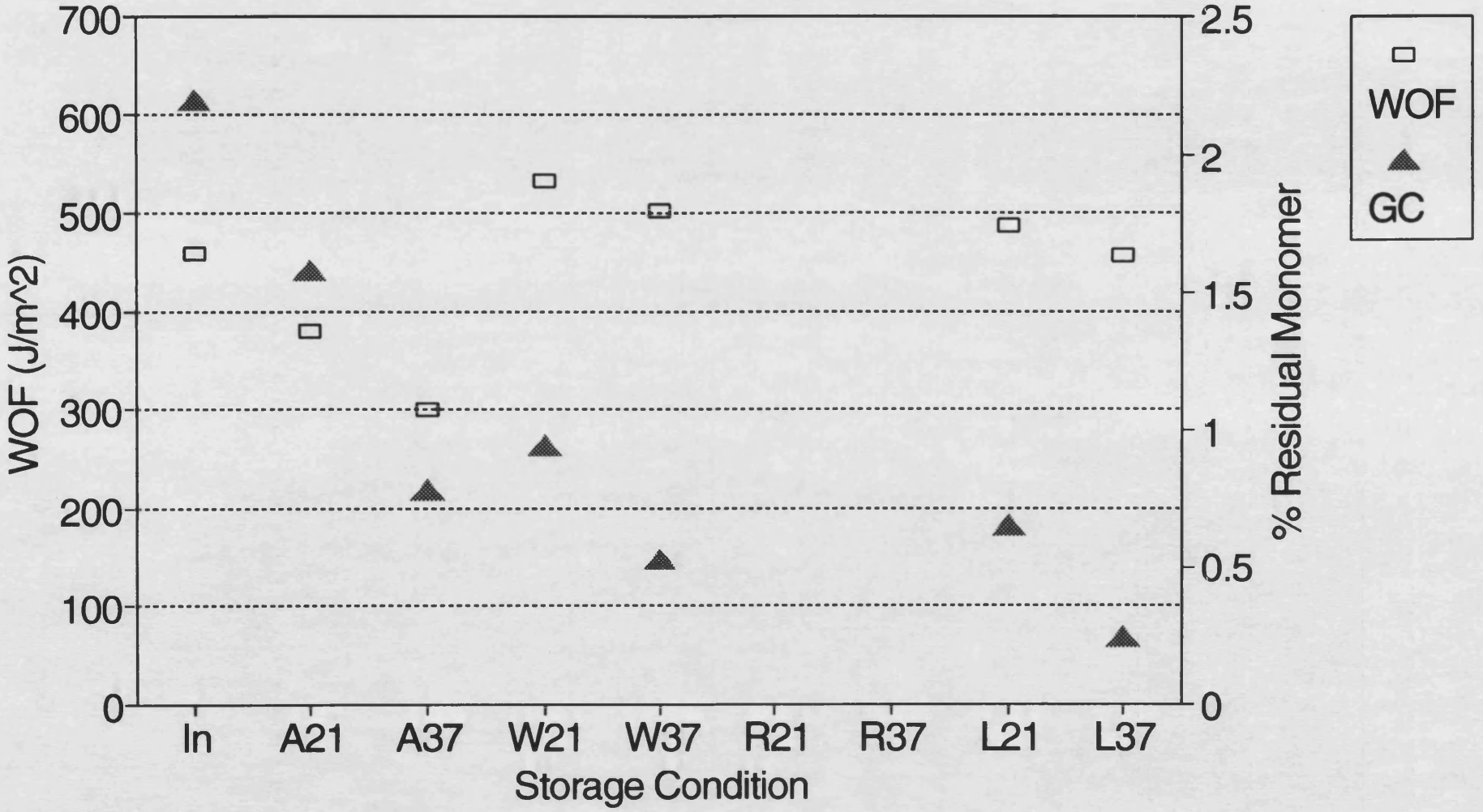


Figure 7.5 : WOF versus GC Results
for Normal Cement after 18 Months

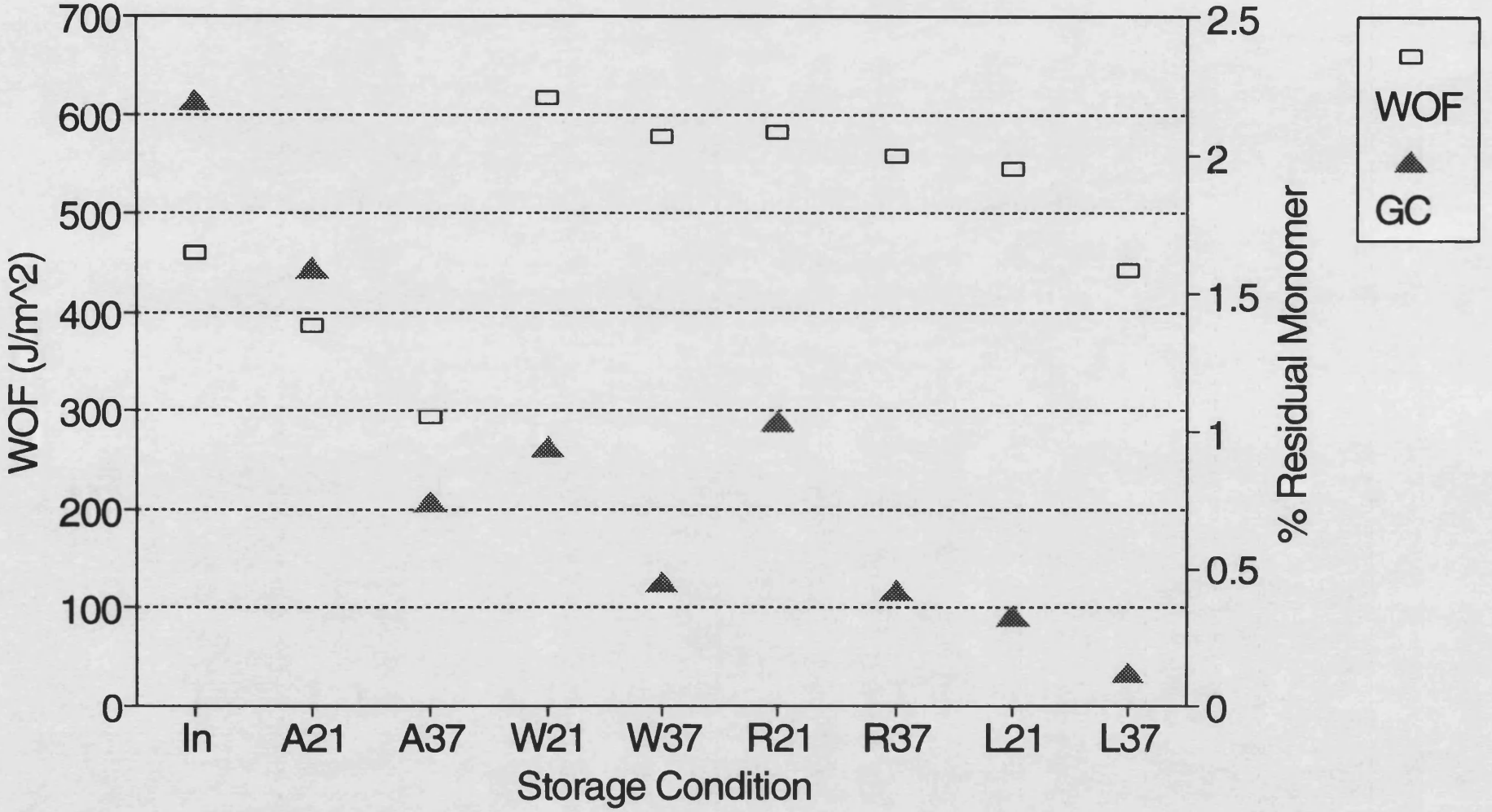
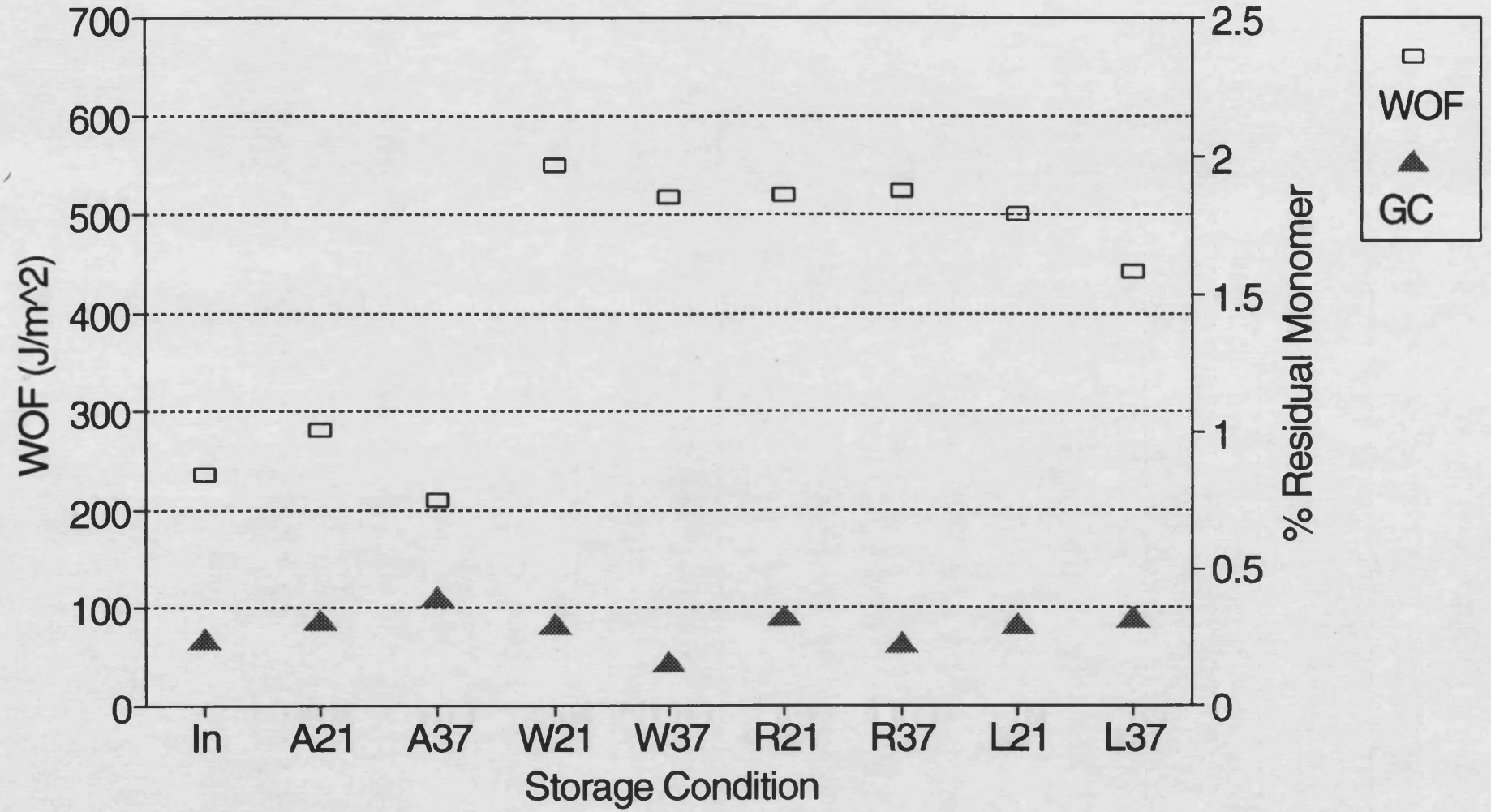


Figure 7.6 : WOF versus GC Results
for Fully Cured Cement after 16 Months



8. MOLECULAR MASS

8.1 Molecular Mass Results

8.1.1 Details of the Presentation of the Results

The graphs of molar mass distributions for samples of normal and fully cured cement after storage under different conditions are shown in Figures 8.1 - 8.16. The number and weight average molecular masses are also summarised in tabular form in Tables 8.1 and 8.2. These tables show the storage condition of the sample, the number of injections, the number average molecular mass, and the weight average molecular mass.

The molecular masses are also shown graphically in two pairs of graphs, one graph in each pair showing the results for samples of normal cement and one showing the results for fully cured cement. On the first pair of graphs (Figures 8.17 and 8.19) the number average molecular masses are superimposed on the mean WOF values for the various storage conditions. These conditions are represented by the letters "In", "A", "W", "R", and "L" which correspond to initial, air, water, Ringer's, and lipid respectively, and by the numbers "21" and "37" which correspond to the two storage temperatures. On the second pair of graphs (shown in Figures 8.18 and 8.20) the weight average molecular masses are superimposed on the mean WOF values. The symbols on these graphs represent the mean WOF and the average molecular mass for the storage condition shown on the x-axis. The WOF is plotted on the normal y-axis (on the left hand side), and the molecular mass is plotted on the second y-axis (on the right hand side). The standard deviations are not shown on any of the graphs to allow easier comparison of the results.

8.1.2 Results for Normal and Fully Cured Cement

The number average and weight average molecular masses of normal and fully cured cement samples are given in Tables 8.1 and 8.2. The number average molecular masses are compared with the WOF results for samples of normal and fully cured

cement in Figures 8.17 and 8.19 respectively. In Figures 8.18 and 8.20 the WOF results are compared with the weight average molecular masses for samples of normal and fully cured cement respectively.

From Figures 8.17 - 8.20 it can be seen that the molecular masses for samples of both types of cement were independent of storage condition. There were no differences in molecular mass for samples stored in the fluids as opposed to in air, nor between samples stored at 21°C and those at 37°C. Hence there was no relationship between the WOF and the molecular mass of the samples. There also appeared to be no differences between the molecular masses of samples of normal cement and those of fully cured cement samples.

Superimposing the molar mass distributions for each of the cement samples studied on top of each other (see Figures 8.1 - 8.16), also did not reveal any differences between any of the treatments.

8.2 Discussion of Molecular Masses

As discussed in section 4.2.1 care must be taken when comparing the molecular masses of dental resins to those of bone cements, as the former generally tend to contain cross linking agents such as ethylene glycol dimethacrylate (Huggett, Bates and Packham, 1983), whereas bone cements are essentially linear polymers (Bargar, Brown, Paul, Voegli, Hseih and Sharkey, 1986).

8.2.1 Molecular Mass Distribution Curves

The molecular mass distribution curves shown in Figures 8.1 - 8.16 were slightly skewed towards the low molecular mass side of the graphs. This effect has also been

shown by Haas, Brauer and Dickson (1975), and Brauer, Termini and Dickson (1977) who all reported that this was typical of free radical polymerised vinyl polymers. Another common feature of the free radical polymerisation process is a broad molecular mass distribution in the resultant polymer (Lautenschlager, Stupp and Keller, 1984, and Black, 1988). This results in both the bead component and the cured cement having a broad molecular mass distribution, as also shown in Figures 8.1 - 8.16.

8.2.2 Molecular Mass of Normal and Fully Cured Cement : Effect of Storage Condition

It can be seen from Tables 8.1 and 8.2 that the average values for the number average molecular mass and the weight average molecular mass, of the bone cement samples produced in this study, were approximately 90,000 and 300,000 respectively. Both these values are a little higher than those quoted in the literature by other workers (Haas, Brauer and Dickson, 1975, Brauer, Termini and Dickson, 1977, and Bayne, Lautenschlager, Compere and Wildes, 1975). The differences between our results and those quoted in the literature have been attributed to variations in mixing technique and curing conditions.

As discussed in section 8.1.2 no gross changes in the molecular masses of samples stored under the different conditions were observed. The small differences observed between occasional samples were of a similar order to the differences one would expect between two separately mixed batches of cement (Price, 1992). From the results of this thesis, it appeared that if hydrolysis of the cement, and chain scission were occurring, it was not on a detectable scale.

Bargar, Brown, Paul, Voegli, Hseih and Sharkey (1986) also reported no difference between the molecular mass of bone cement which had been stored in air and that which had been stored in water for up to 8 weeks. Although this supports our results, it

is unlikely that any chain scission would have occurred in such a short storage time. However, in a study on samples of bone cement which were obtained during revision surgery, Eyerer and Jin (1986) showed that there was no change in the molecular mass of the cement with implantation time. The authors found that samples of Palacos R and Sulfix 6 which had been implanted for up to 14 years had similar molecular masses to samples which had been freshly prepared *in vitro*. Thus it was concluded that the chemical decomposition observed with other implantable polymers, such as polyethylene, does not occur in acrylic bone cement. Therefore it is unlikely that any degradation such as chain scission (and a reduction in the molecular mass) occurred with our samples of bone cement over the 18 month time period studied.

Since there was no change in the molecular mass of the cement with storage under the various conditions, there was no relationship between the WOF of the cement and its molecular mass. It has been previously reported that for PMMA with a weight average molecular mass greater than 100,000, the mechanical properties of the material are independent of molecular mass (Martin, Johnson and Cooper, 1973). The weight average molecular mass of the cement tested in this study was approximately 300,000, therefore any minor variations in molecular mass would not influence the WOF of the cement.

8.2.3 Molecular Mass of Normal and Fully Cured Cement : Dependence on Heat Treatment

Within experimental error it appeared, from the results of this thesis, that there was no difference between the molecular mass of the normal cement and that of the fully cured cement.

The results of Huggett, Bates and Packham (1987) suggested that curing a dental acrylic in water at 70°C for 14 hours produced a polymer with a higher molecular mass than the same resin cured in boiling water for 30 minutes. Bevan and Earnshaw

(1968) also suggested that variations in the curing temperatures of different acrylic dental resin systems would produce specimens with different molecular masses. This was not, however, evident from our study of the molecular mass of normal and fully cured (heat treated) bone cement specimens. From our results it appeared that both the normal and the fully cured cement samples had similar molecular masses.

Beech (1975) has shown for dental resins, that it is the temperature at the beginning of the curing cycle which is the most important factor in controlling the final molecular mass of the polymer. In this thesis the fully cured cement was heat treated after it had set. Thus the temperature at the beginning of the curing cycle was the same for both types of cement, which could explain the similarity of their molecular masses.

8.3 Summary of Molecular Mass

There was no relationship between the WOF and the molecular mass of the cement samples tested in this study. Also the molecular mass of bone cement was not influenced by its storage environment, and did not appear to change with time. This suggests that it is unlikely that any degradation such as chain scission occurs with acrylic bone cement. Thus the long-term mechanical stability of the material will not deteriorate *in vivo* as a result of chemical decomposition.

Table 8.1 : Molecular Mass Results for Normal Bone Cement Samples

Storage Condition	No. of Injections	Number Average Mol. Wt. (M_n)	Weight Average Mol. Wt. (M_w)
Initial	1	111680	303040
553D-A21°C	1	75381	300460
553D-A37°C	1	94037	283130
553D-W21°C	1	75566	304650
553D-W37°C	1	84542	288390
553D-L21°C	1	79979	290220
553D-L37°C	1	73532	296030

NOTES

i) Initial corresponds to samples 30 minutes after curing.

ii) 553D corresponds to 553 days (18 months).

iii) A21°C corresponds to air at 21°C. W, R, and L correspond to water, Ringer's, and lipid respectively.

iv) Molecular masses are accurate to ±5%.

Table 8.2 : Molecular Mass Results for Fully Cured Bone Cement Samples

Storage Condition	No. of Injections	Number Average Mol. Wt. (M_n)	Weight Average Mol. Wt. (M_w)
Initial	1	99939	304260
455D-A21°C	1	89563	288970
455D-A37°C	1	87366	285580
455D-W21°C	1	67338	277420
455D-W37°C	1	95686	296900
455D-R21°C	1	113210	316610
455D-R37°C	1	65453	289530
455D-L21°C	1	74219	282380
455D-L37°C	1	79124	280550

NOTES

i) Initial corresponds to samples 30 minutes after heat treatment.

ii) 455D corresponds to 455 days (15 months).

iii) A21°C corresponds to air at 21°C. W, R, and L correspond to water, Ringer's, and lipid respectively.

iv) Molecular masses are accurate to ±5%.

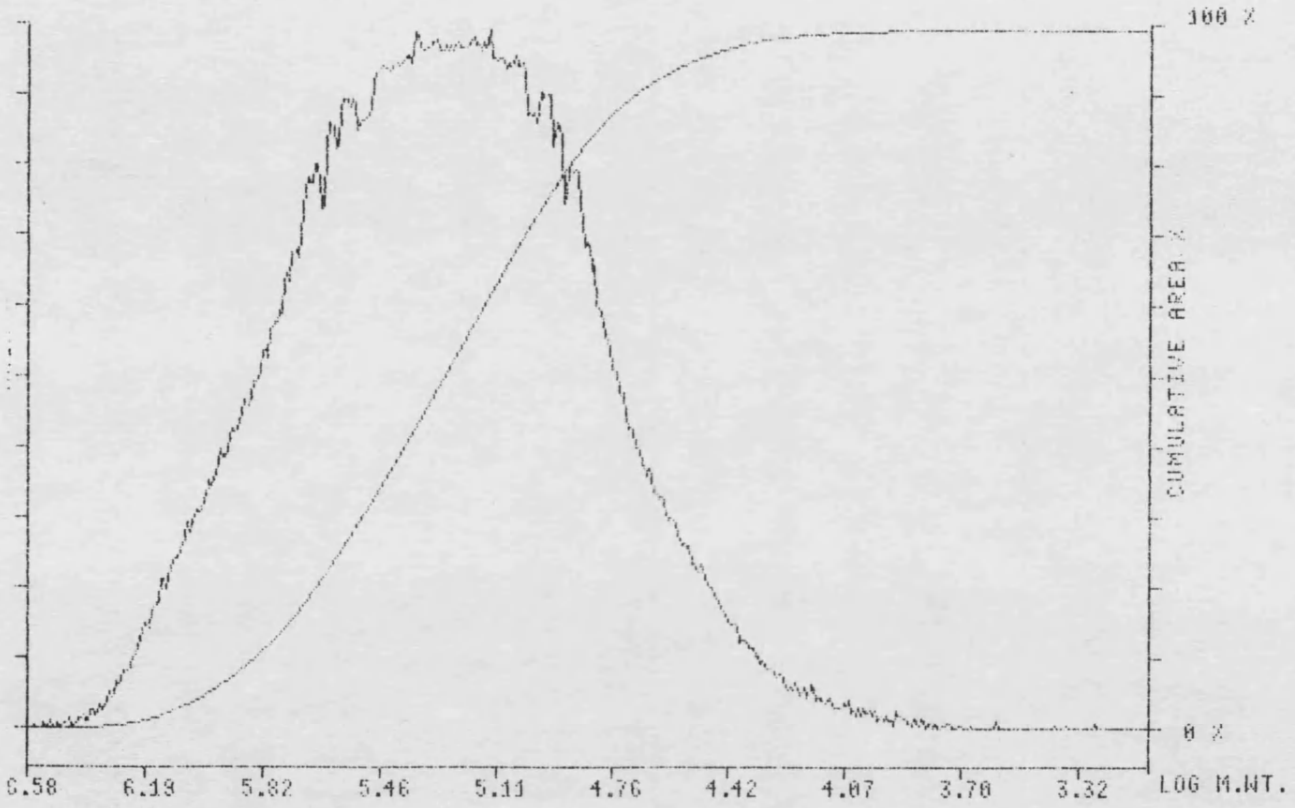


Figure 8.1 : Molecular Mass Distribution for a Sample of Normal Cement Tested Immediately (30 minutes) After Curing.

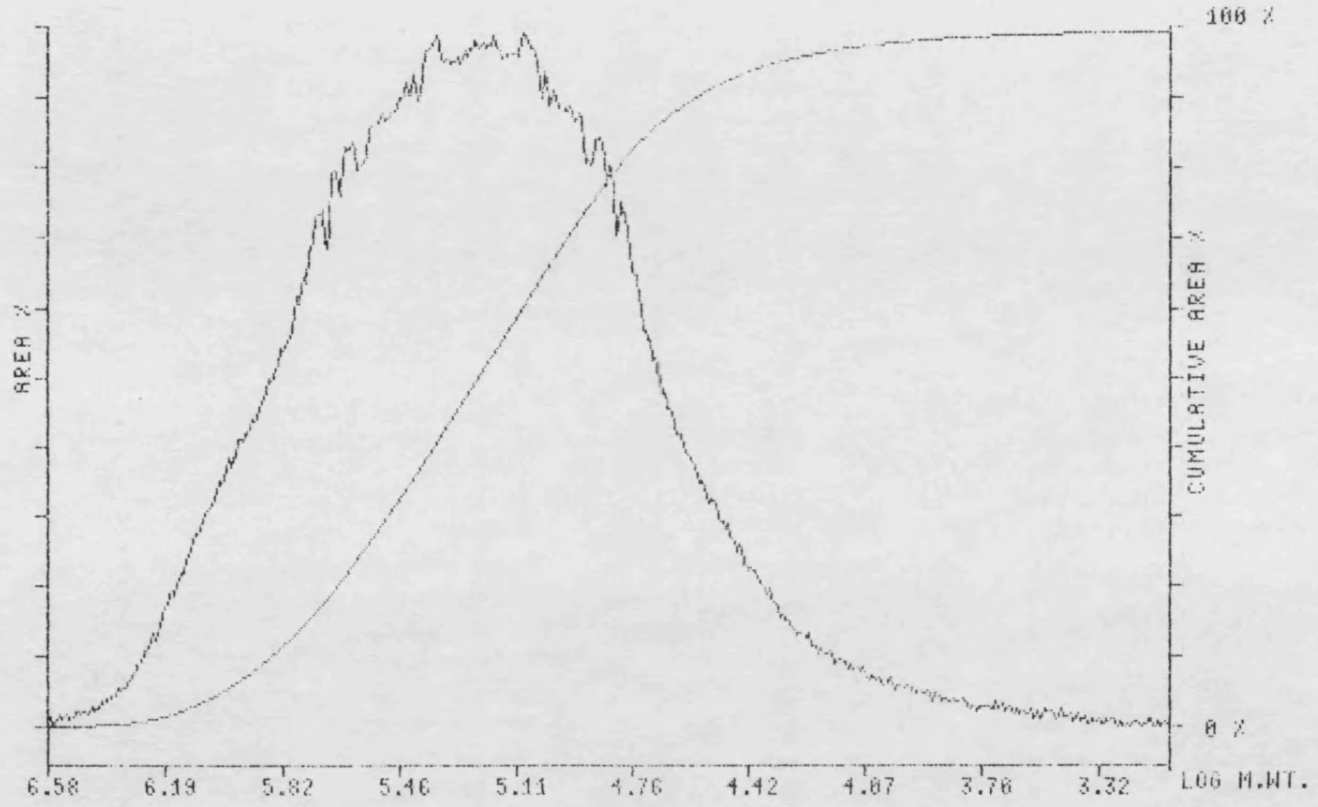


Figure 8.2 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Air at 21°C for 18 Months.

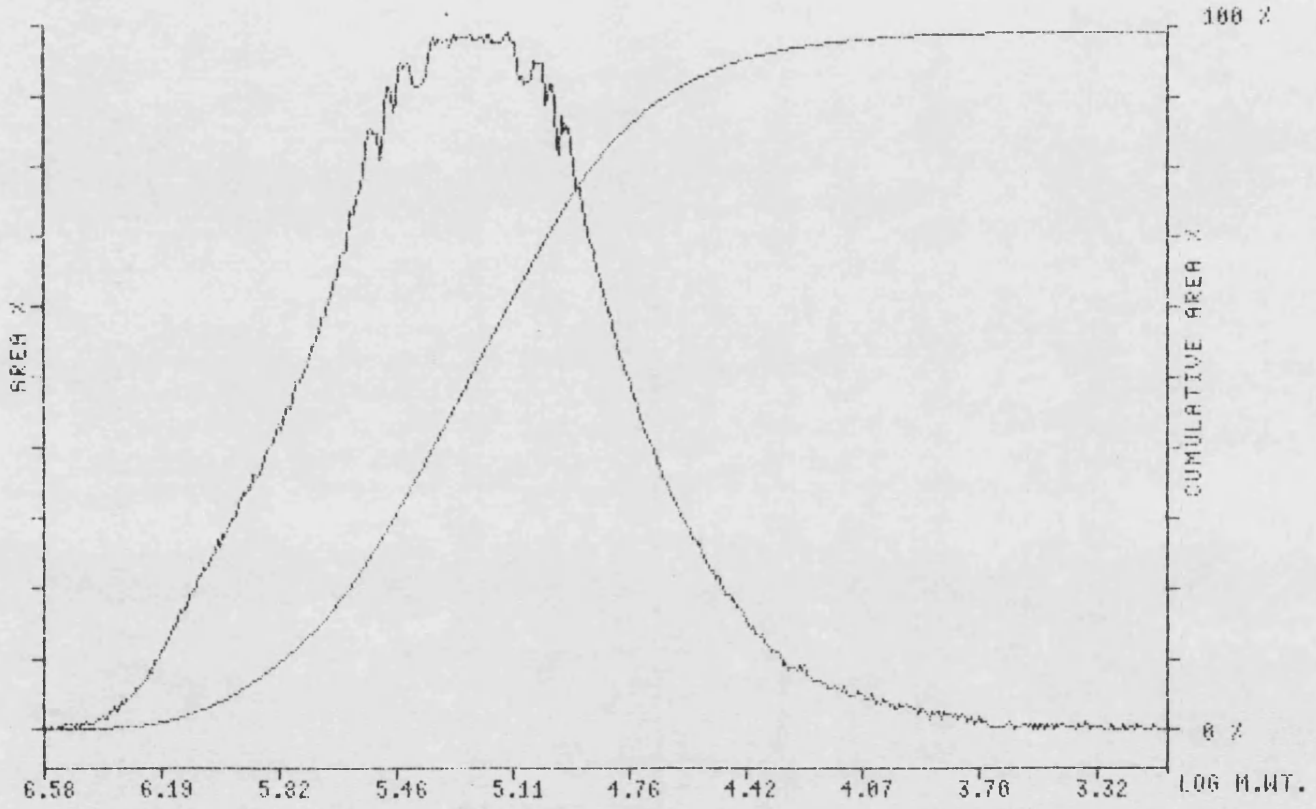


Figure 8.3 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Air at 37°C for 18 Months.

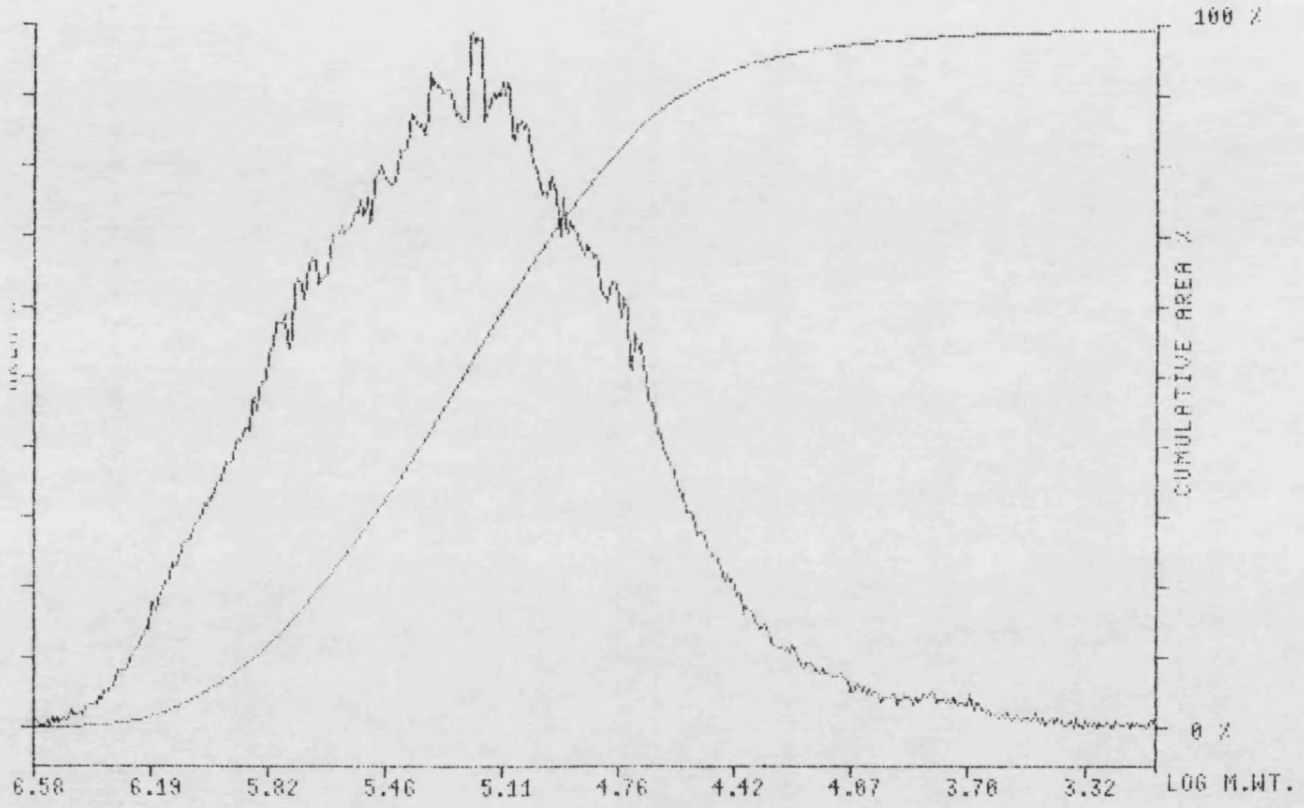


Figure 8.4 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Water at 21°C for 18 Months.

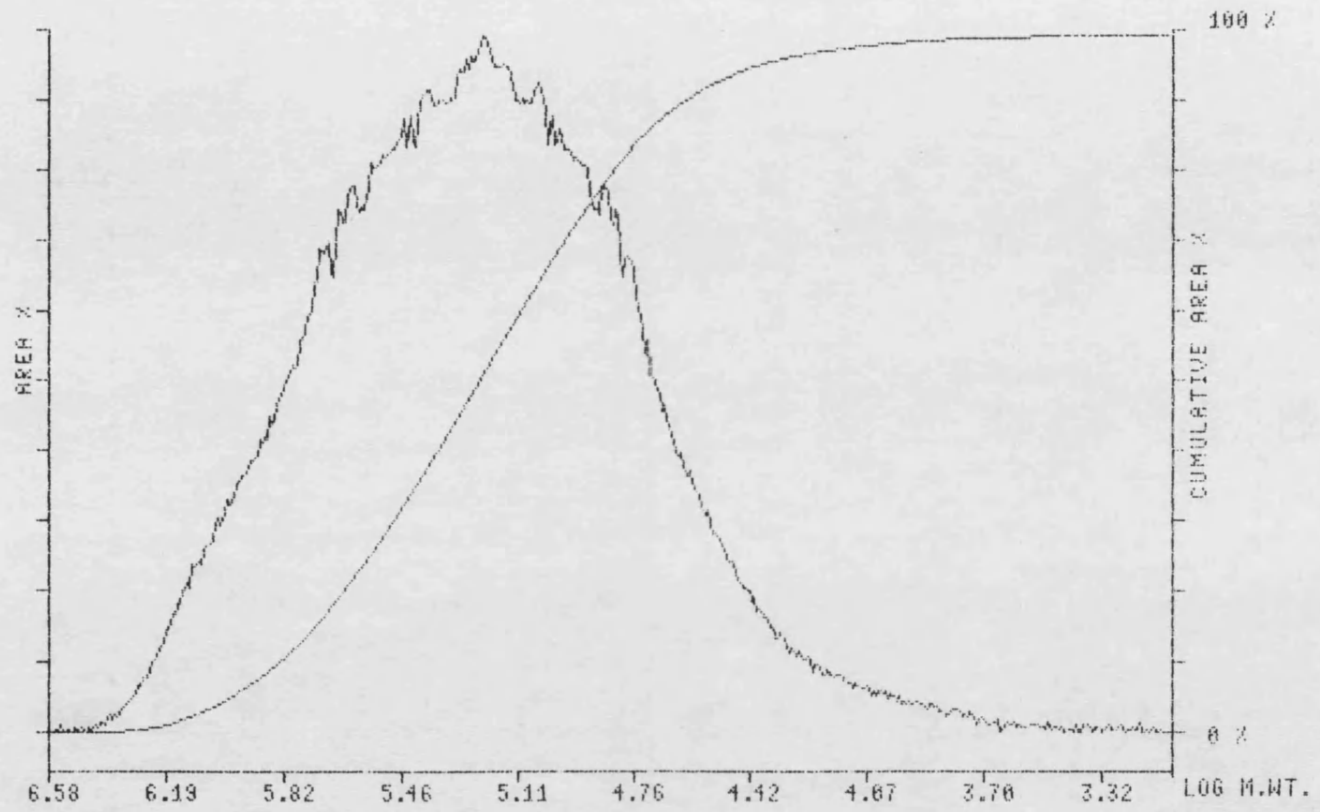


Figure 8.5 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Water at 37°C for 18 Months.

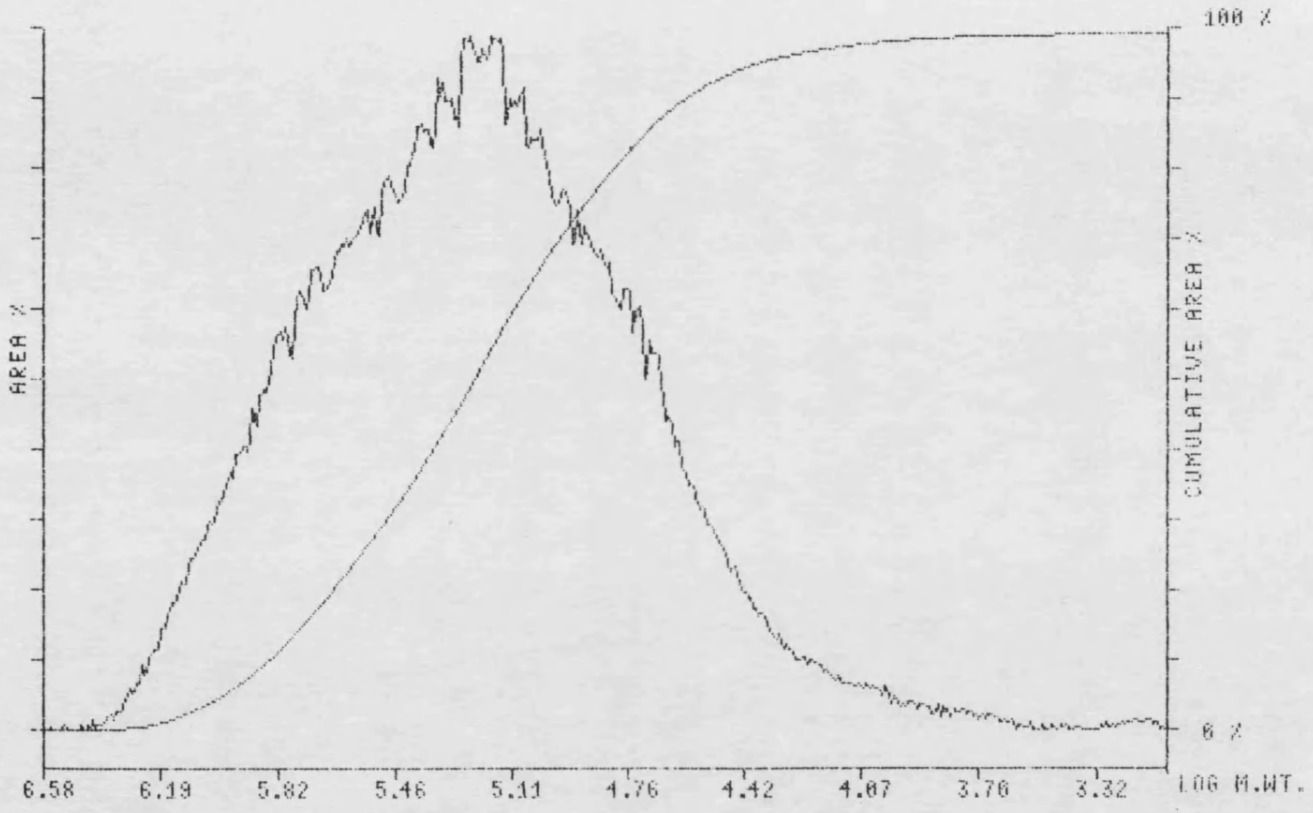


Figure 8.6 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Lipid at 21°C for 18 Months.

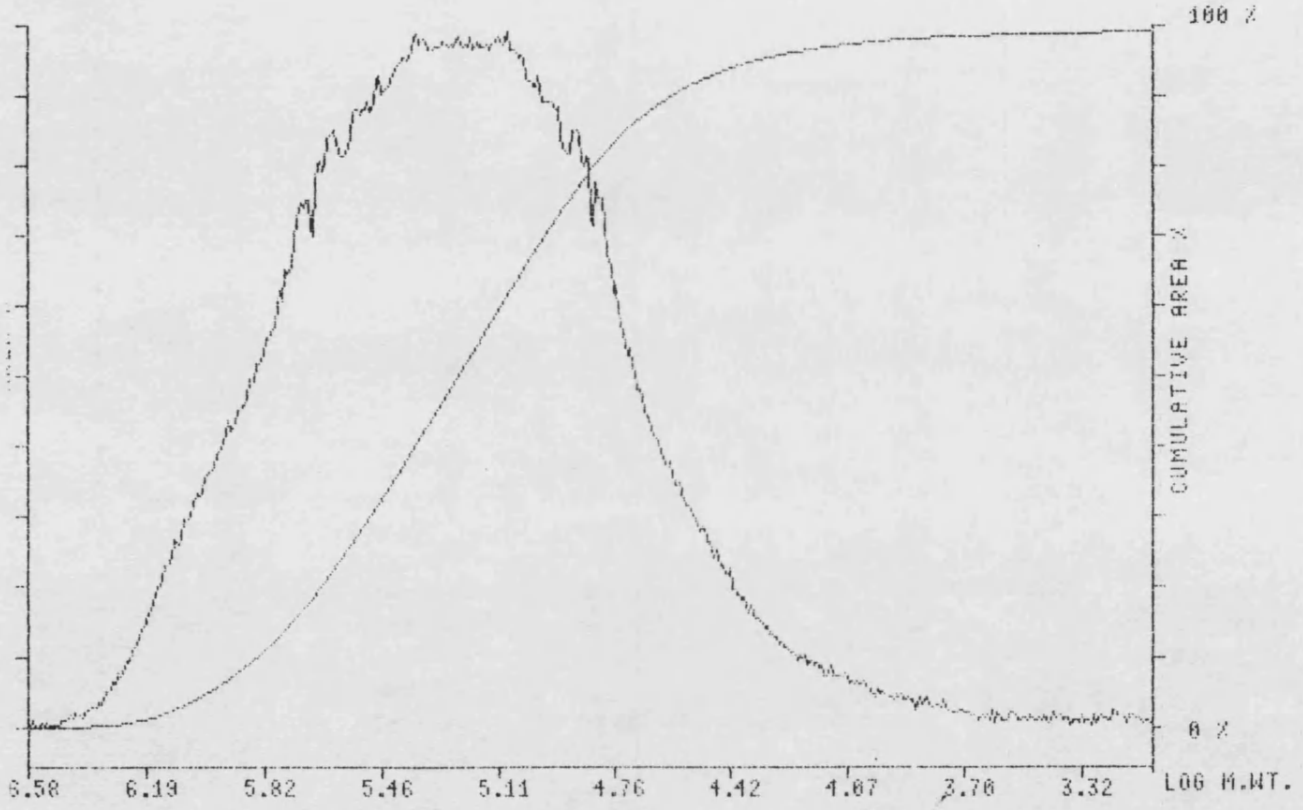


Figure 8.7 : Molecular Mass Distribution for a Sample of Normal Cement After Storage in Lipid at 37°C for 18 Months.

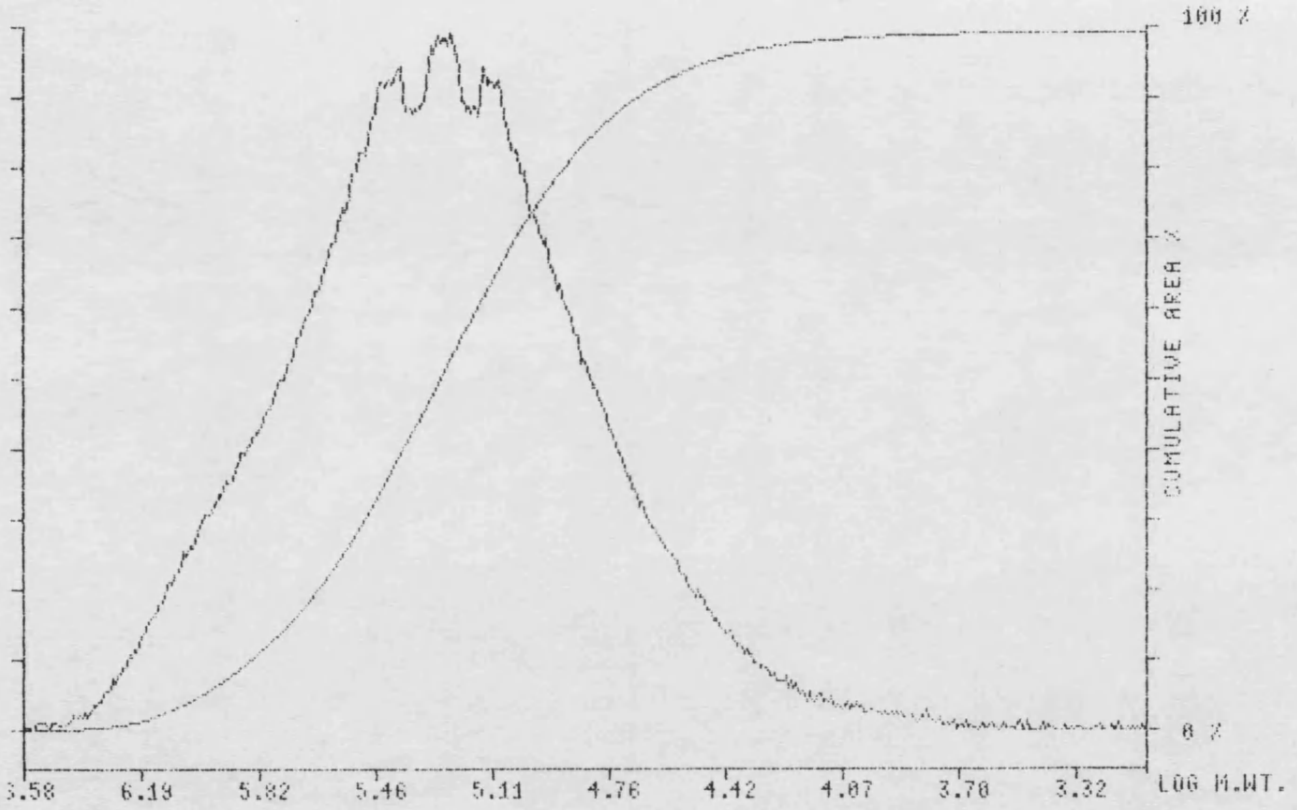


Figure 8.8 : Molecular Mass Distribution for a Sample of Fully Cured Cement Tested Immediately (30 minutes) After Heat Treatment.

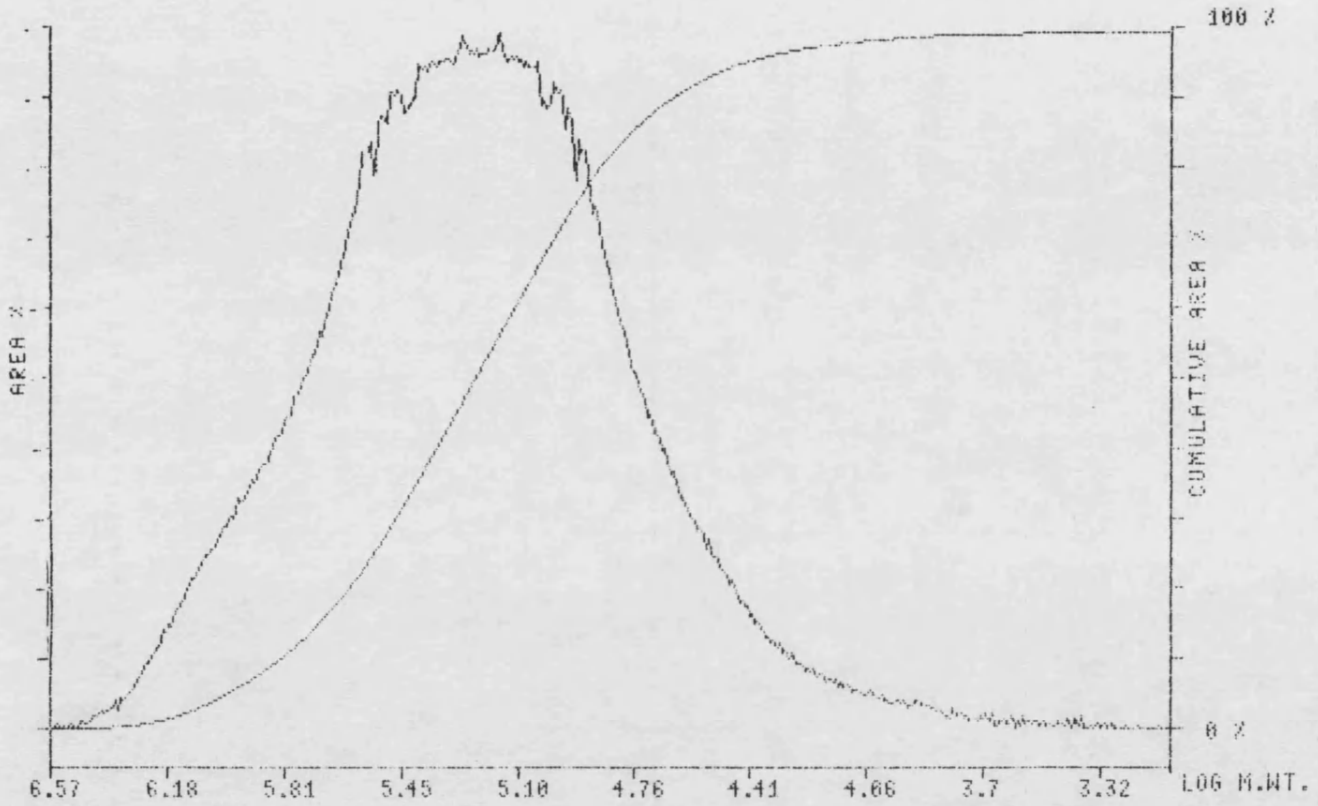


Figure 8.9 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Air at 21°C for 16 Months.

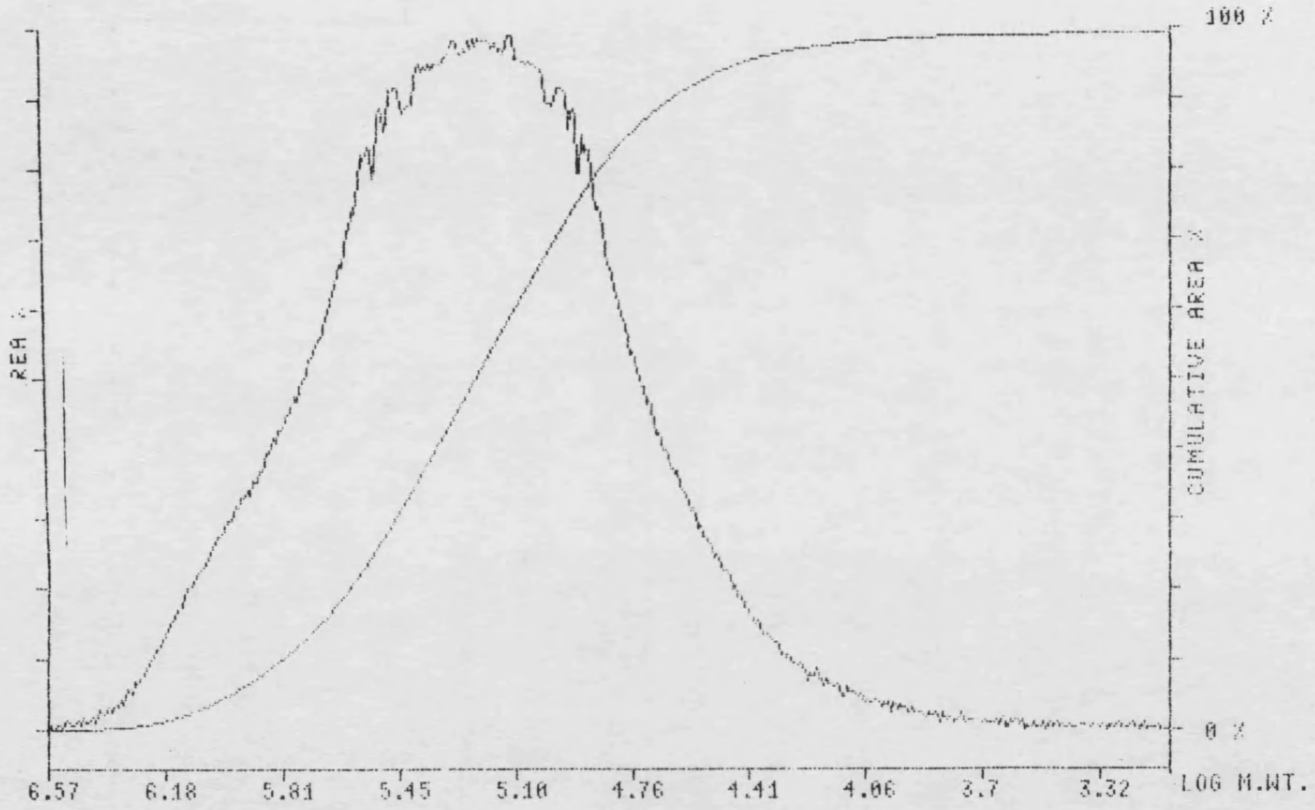


Figure 8.10 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Air at 37°C for 16 Months.

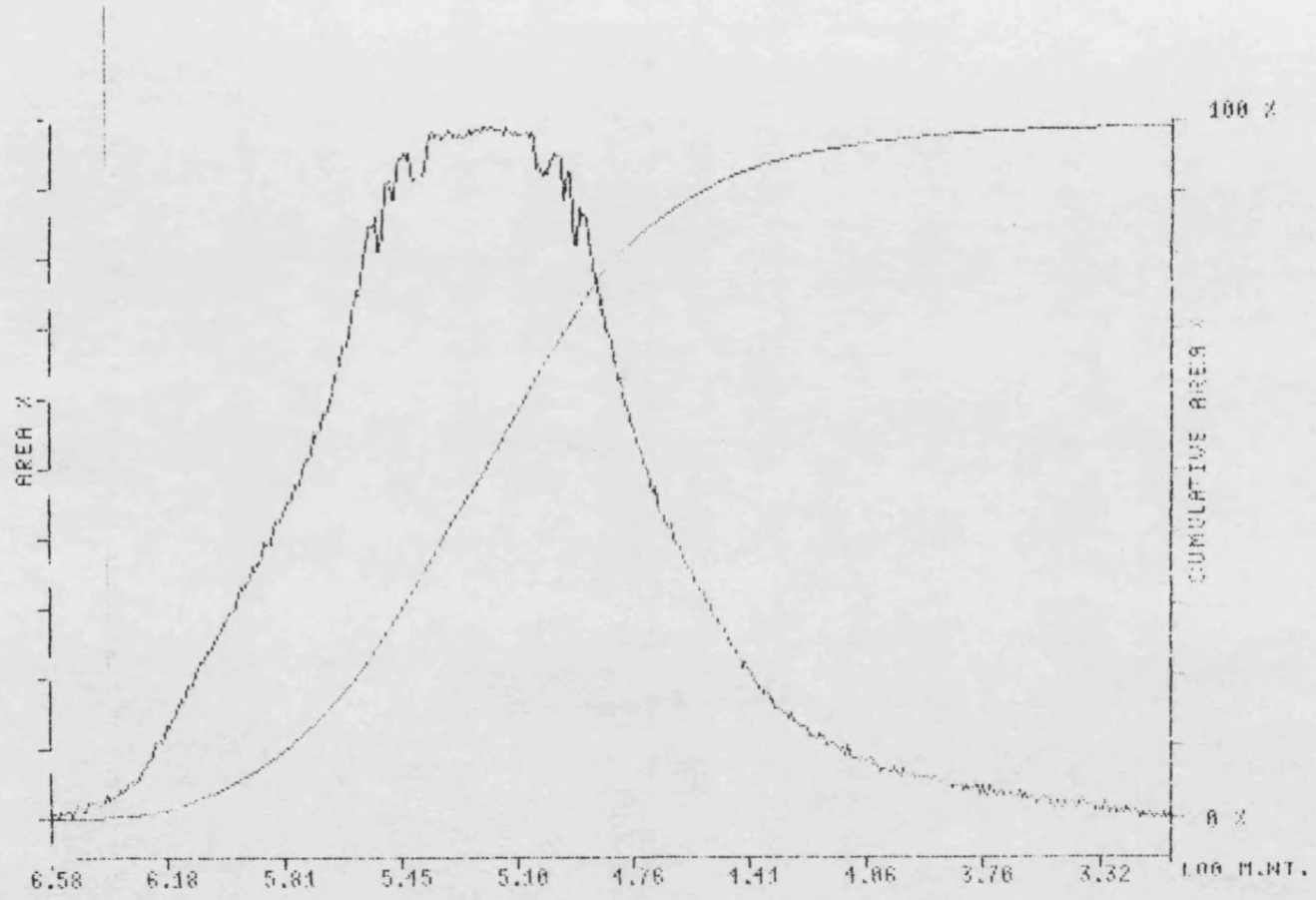


Figure 8.11 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Water at 21°C for 16 Months.

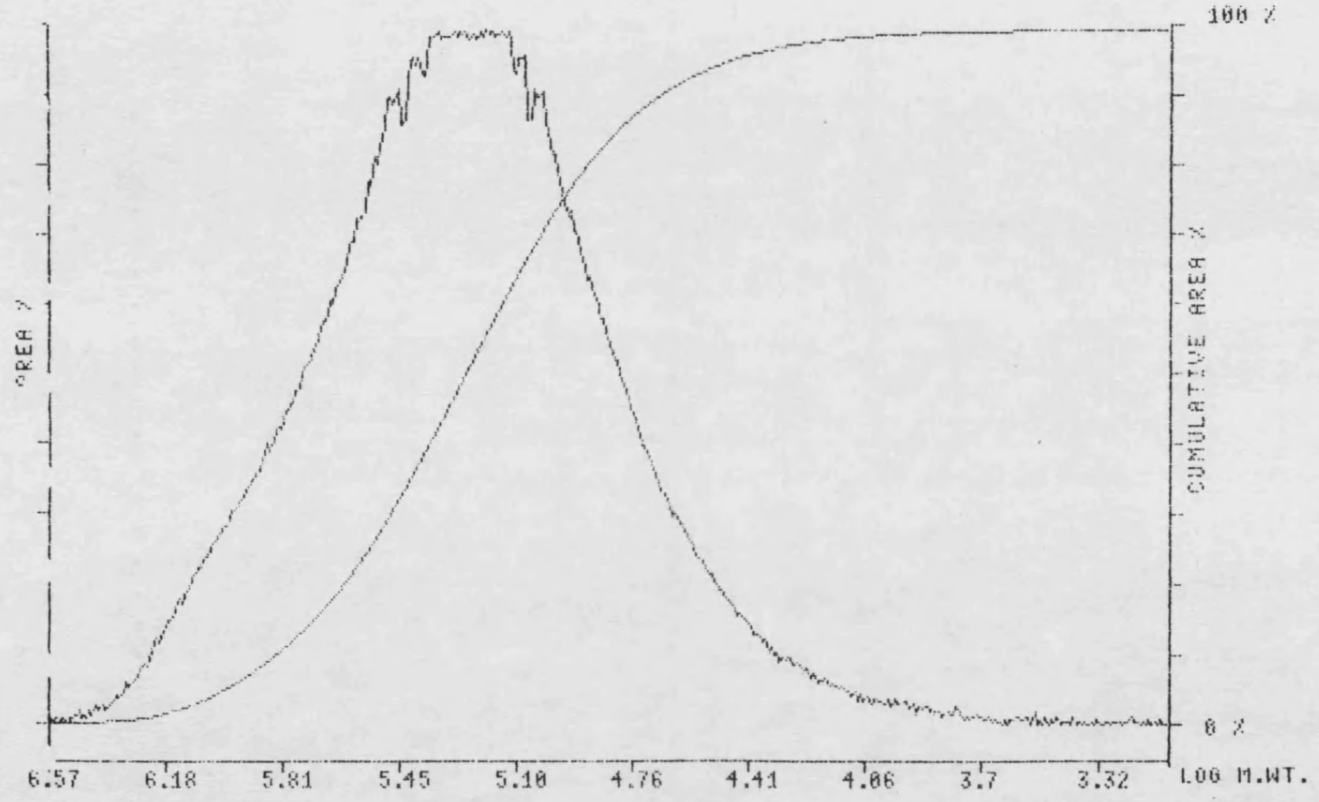


Figure 8.12 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Water at 37°C for 16 Months.

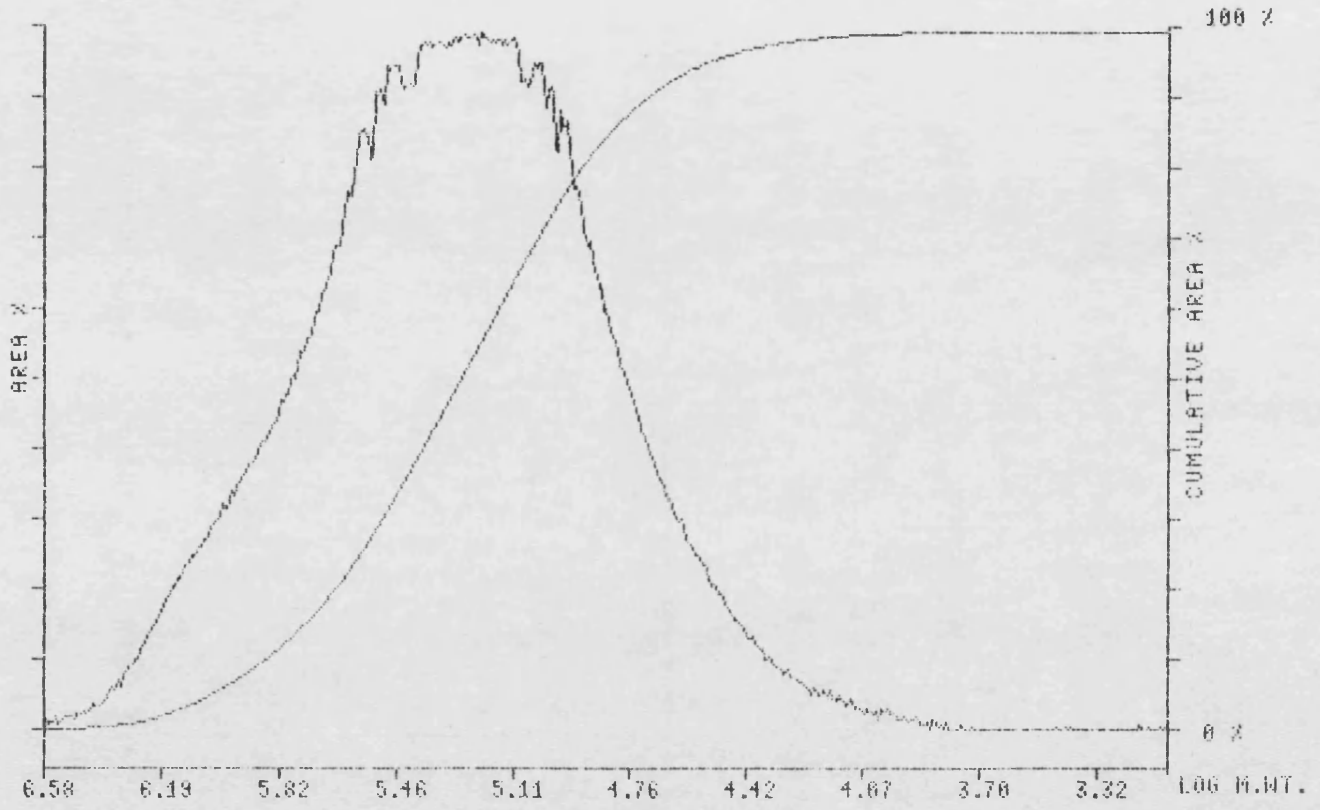


Figure 8.13 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Ringer's at 21°C for 16 Months.

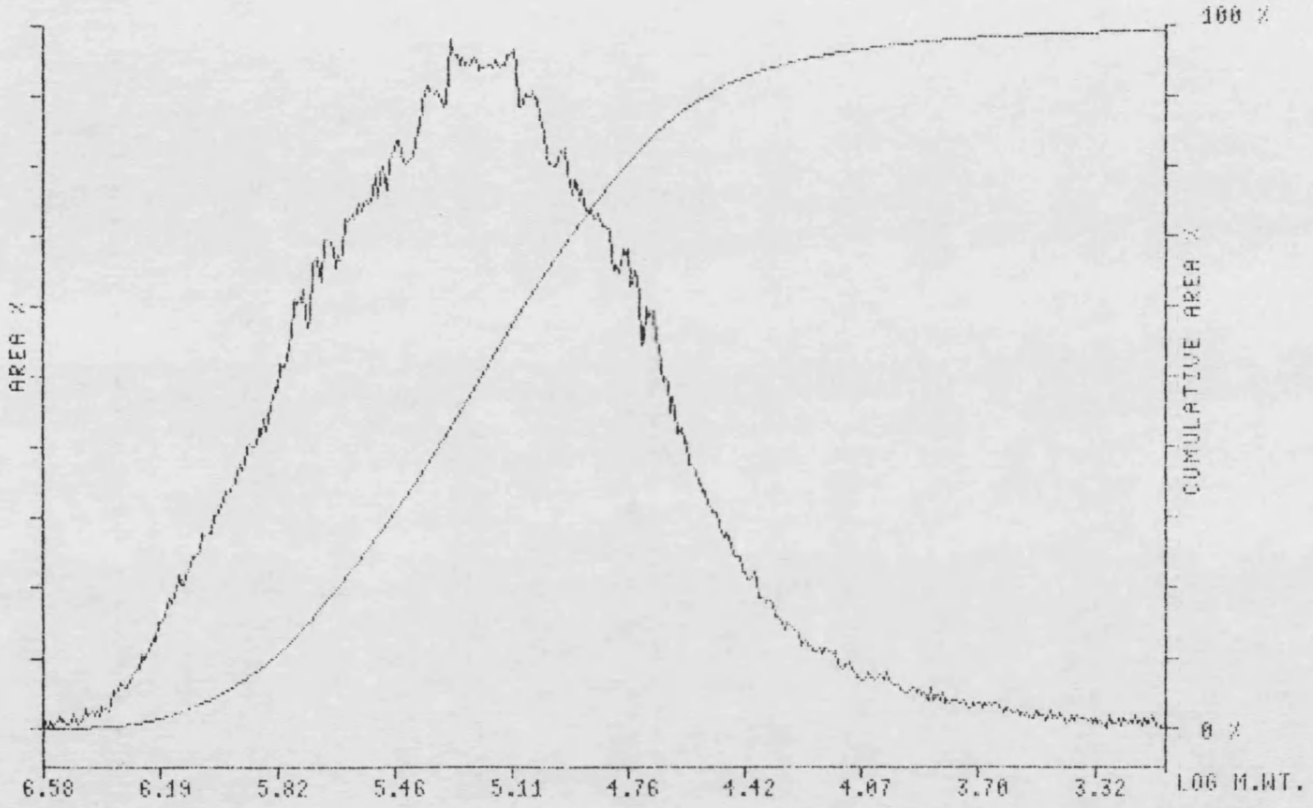


Figure 8.14 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Ringer's at 37°C for 16 Months.

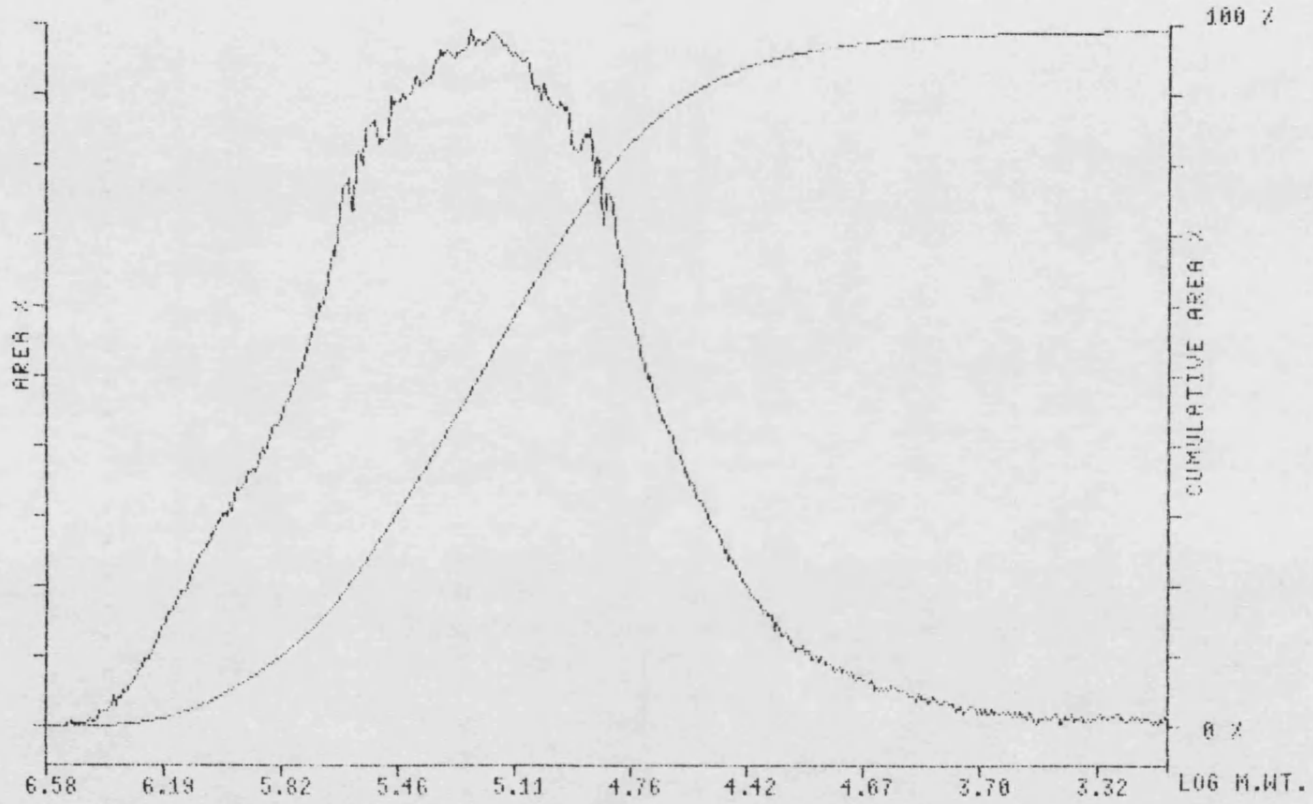


Figure 8.15 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Lipid at 21°C for 16 Months.

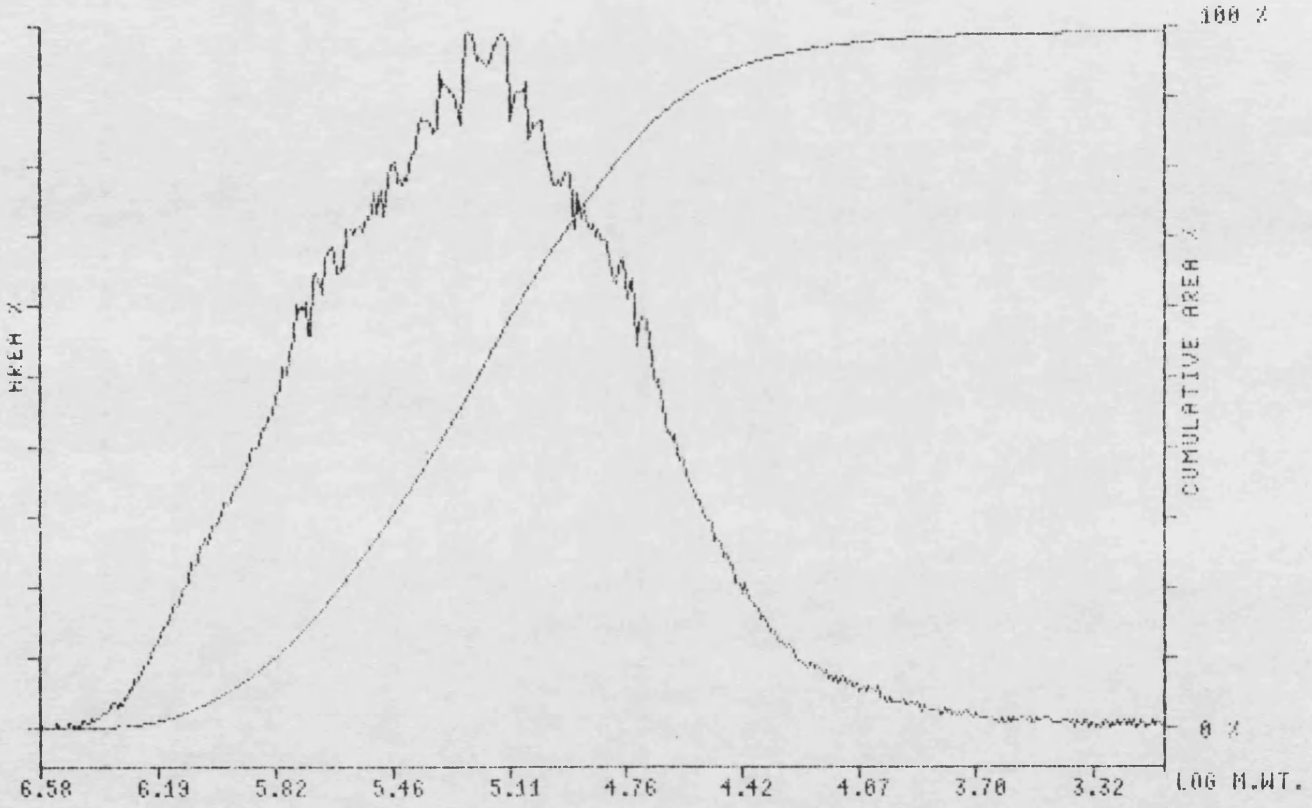


Figure 8.16 : Molecular Mass Distribution for a Sample of Fully Cured Cement After Storage in Lipid at 37°C for 16 Months.

Figure 8.17 : WOF Results versus Mn for Normal Cement after 18 Months

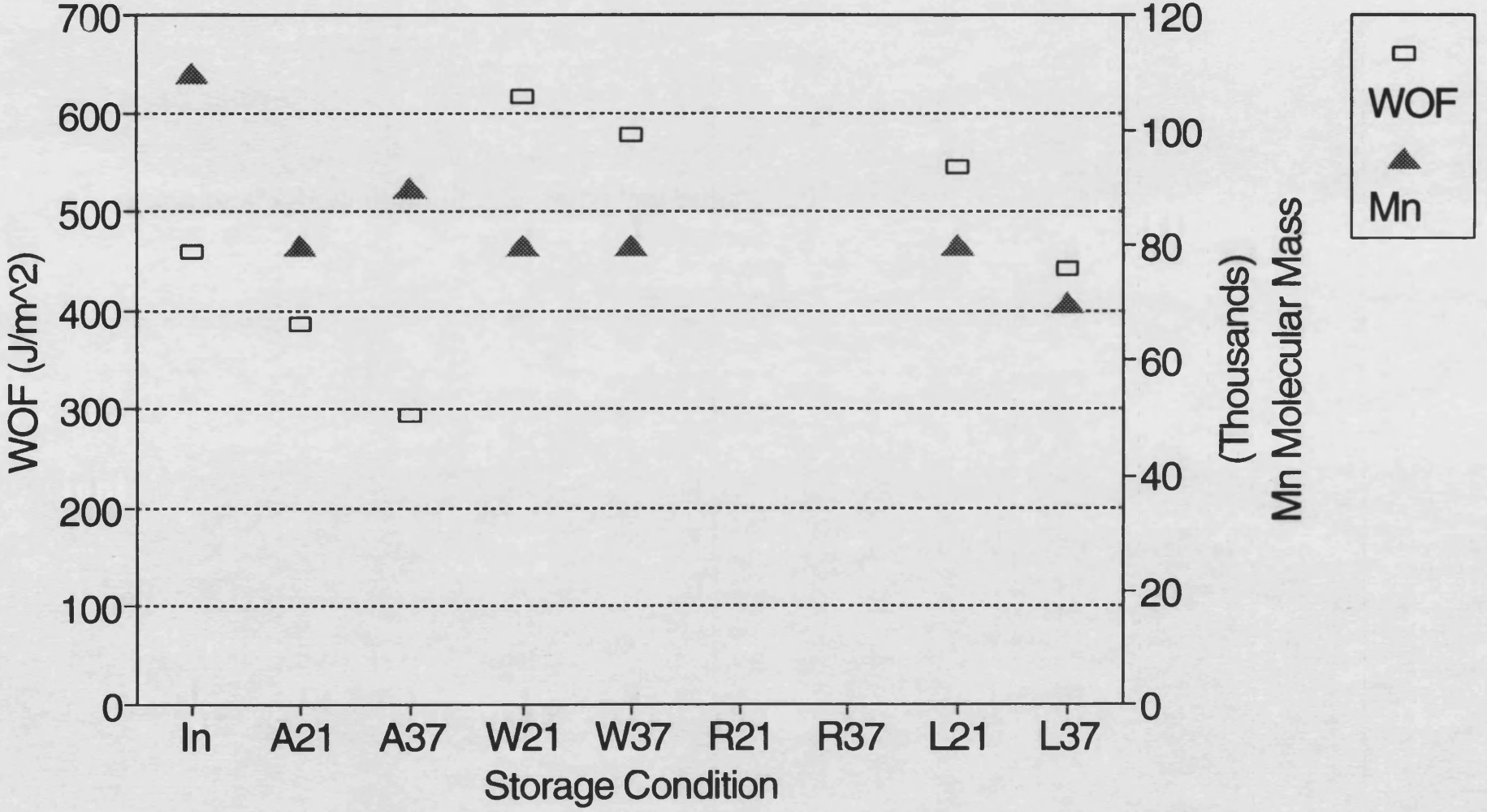


Figure 8.18 : WOF Results versus Mw
for Normal Cement after 18 Months

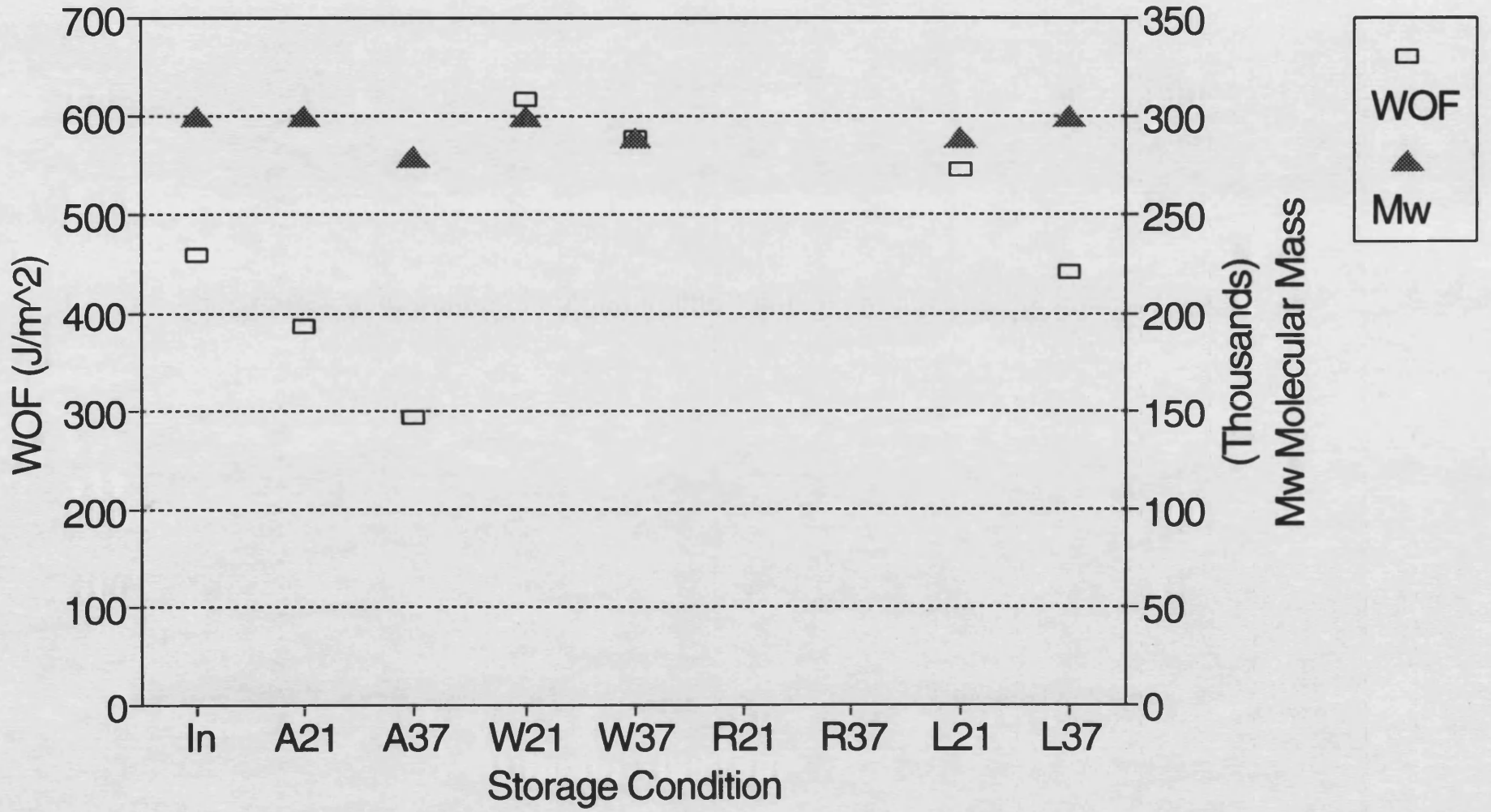


Figure 8.19 : WOF Results versus Mn
for Fully Cured Cement after 16 Months

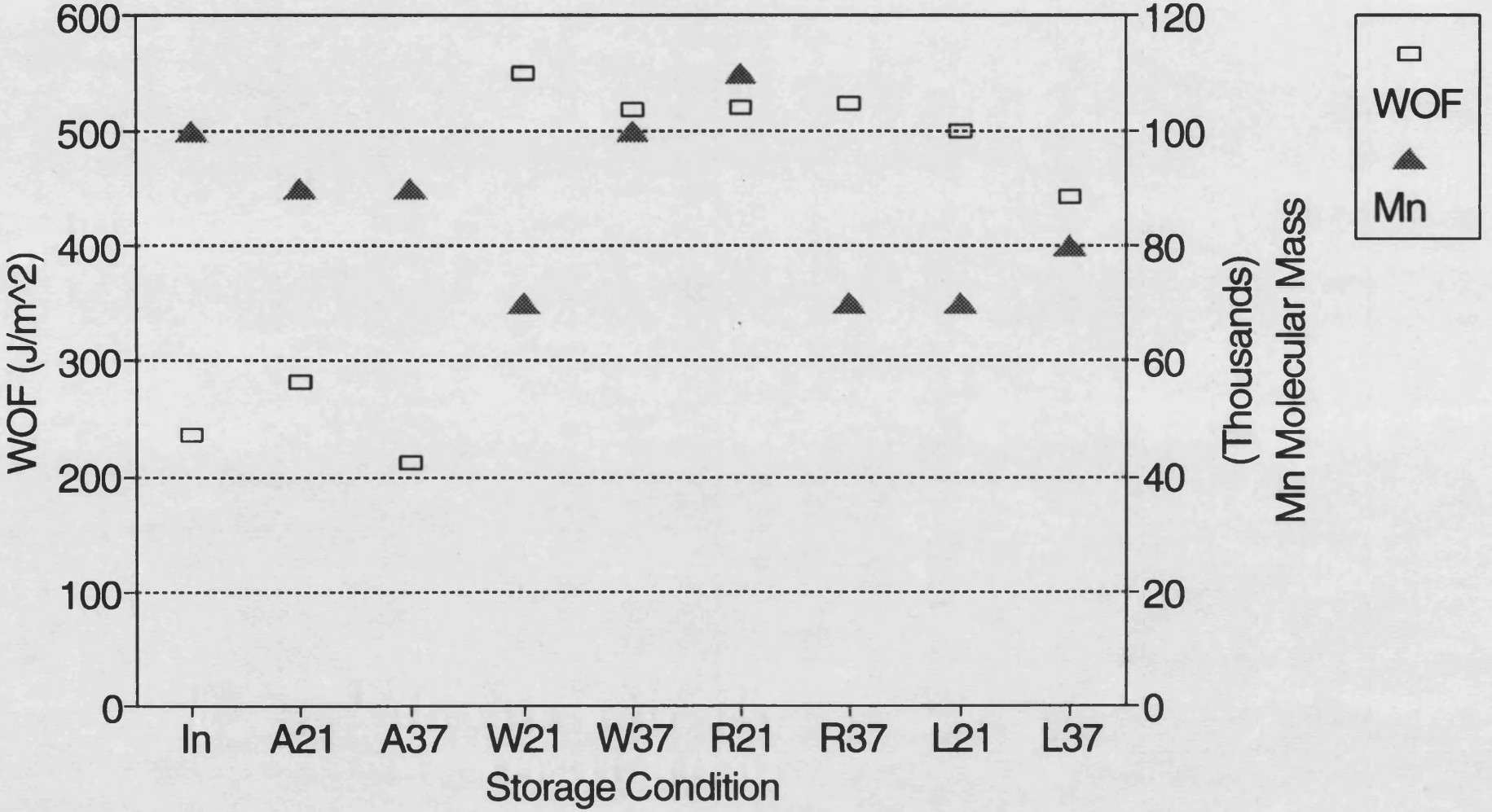
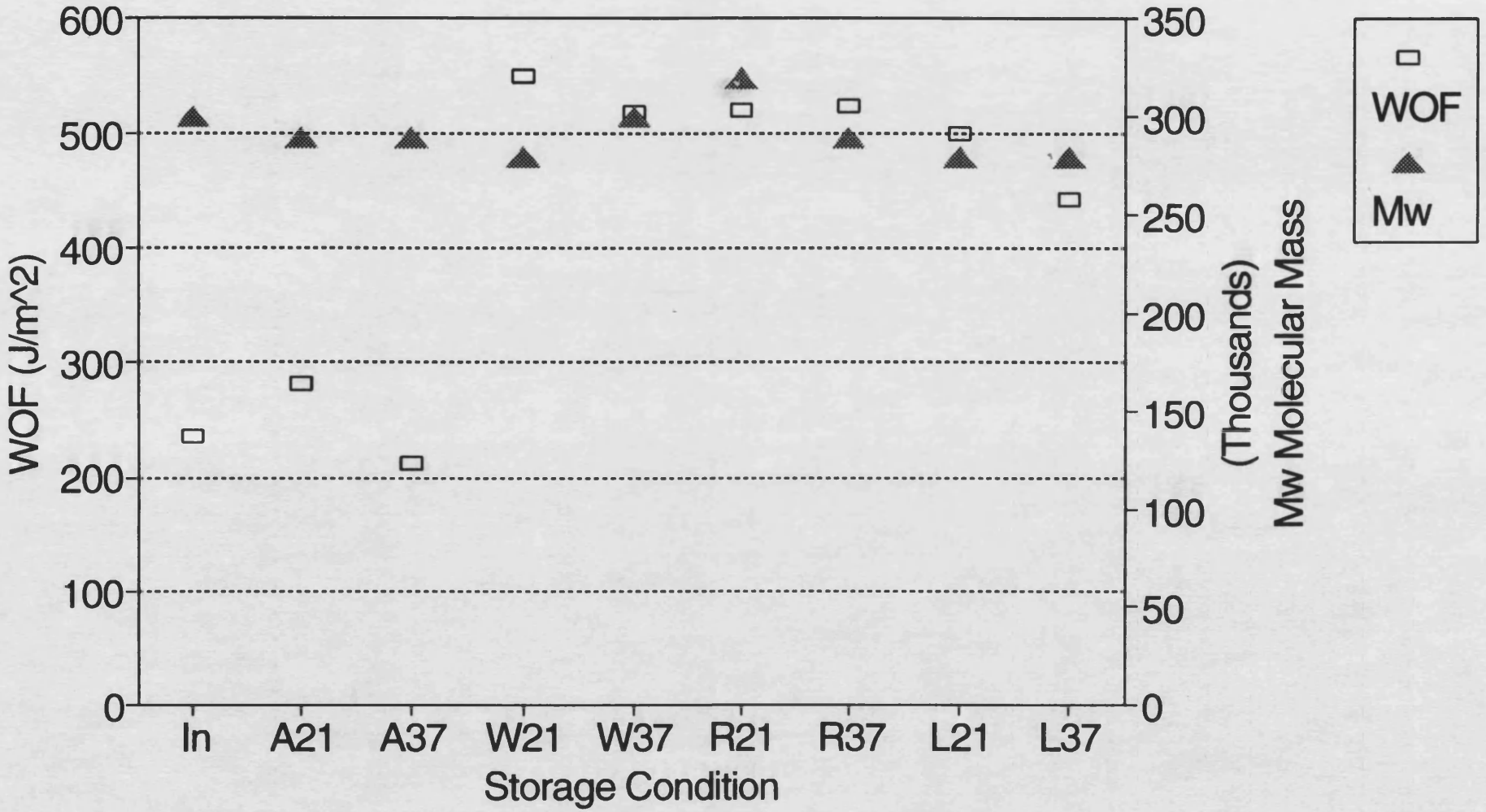


Figure 8.20 : WOF Results versus Mw
for Fully Cured Cement after 16 Months



9. MICROSCOPY

9.1 Cement Powder

Figure 9.1 shows a series of scanning electron micrographs of Simplex P radiopaque bone cement powder at different magnifications. From these micrographs it can be seen that the cement powder was composed of smooth spherical beads, which ranged from under 10μm to over 100μm in diameter, and a powder of finer particles a little less than 1μm in size. The larger beads were the pre-polymerised polymethylmethacrylate (PMMA) component of the cement. It was initially thought that the smaller particles were barium sulphate ($BaSO_4$), the radiopaque agent of the cement. However, a similar fine powder was also found in the radiolucent version of Simplex bone cement, which contains no radiopaque agent, (see Figure 9.2). There were less of the smaller particles in the radiolucent cement, indicating that this fine powder was in part composed of $BaSO_4$. Comparing Figures 9.1 and 9.2, no difference was observed between the smaller particles in either sample of cement. Therefore a sample of isolated barium sulphate was obtained from Howmedica International and examined, as shown in Figure 9.3. There were no differences in the morphology of the sub-micron particles from any of the three samples of powder (Figures 9.1 - 9.3). It was therefore assumed that the small particles in the radiolucent cement were a very fine powder of PMMA, and that the small particles in the radiopaque cement were a mixture of this fine PMMA powder and barium sulphate particles.

9.2 Cured Cement

Optical microscopy of polished sections of the cured cement showed that it was a composite material, consisting of the pre-polymerised PMMA beads embedded in a recently polymerised PMMA matrix. This two phase structure was evident in both the

radiopaque and the radiolucent cements shown in Figures 9.4 and 9.5 respectively. There was little difference between the structure of the two types of Simplex cement, however, a fine dispersion of barium sulphate particles could be seen throughout the matrix of the radiopaque material (see Figure 9.4). These micrographs show the barium sulphate as small individual particles evenly distributed throughout the recently polymerised PMMA matrix. In contrast to the rough barium sulphate impregnated matrix of the radiopaque cement, Figure 9.5 shows that the matrix of the radiolucent cement was instead very smooth and featureless. Both the pre-polymerised PMMA beads and the barium sulphate particles appeared to be well bonded to the matrix, with no evidence of a gap at the interfaces between either bead or particle and the matrix.

There was some porosity in the samples of cured Simplex cement, as shown in Figure 9.6. The pores tended to be irregularly shaped due to the presence of beads around the edges of the pores, and were thought to be due to either air entrapment during mixing, or to the evaporation of pockets of trapped methylmethacrylate monomer during curing.

9.3 Fractography

9.3.1 Fracture Surfaces of Normal Radiolucent Cement from WOF Tests

The fracture surfaces of several radiolucent specimens from a previous study (Watson, Miles, and Clift, 1990) were examined. In this study specimens of radiolucent Simplex P bone cement were stored in air and water at both 21°C and 37°C for 1 and 3 weeks before the WOF was evaluated. Upon examination of these specimens it was apparent that there was little difference in the appearance of the fracture surfaces for the two storage media, although a slight difference between the two storage temperatures was

observed. In general, the specimens stored at 21°C appeared to be rougher and more deformed than the specimens stored at 37°C, which was in agreement with the work of fracture results, where the specimens stored at 37°C were more brittle than those stored at 21°C. This is illustrated in Figures 9.7 and 9.8 which show the fracture surfaces of specimens stored for 1 week in water at 37°C (WOF of 348J/m^2) and 1 week in water at 21°C (WOF of 686J/m^2) respectively.

There was a great deal of directionality to the deformation on the fracture surface of the higher WOF specimen shown in Figure 9.8. These features included areas where material appeared to have rolled up, and bands of lines which could have been crazes. The smoother fracture surface, shown in Figure 9.7, revealed evidence of the pre-polymerised beads beneath the surface. It appeared that the beads had actually been fractured, a detail which was lost on the rougher samples due to the more deformed fracture surface.

9.3.2 Fracture Surfaces of Normal Radiopaque Cement from WOF Tests

Figures 9.9 - 9.13 show scanning electron micrographs of the fracture surfaces of radiopaque test specimens from the Tattersall-Tappin tests performed in this study (WOF ranged from 300 - 650J/m^2). Comparing these micrographs with those for the radiolucent fracture surfaces, shown in Figures 9.7 and 9.8, it can be seen that the addition of barium sulphate led to much rougher, more deformed fracture surfaces. The radiopaque surfaces (Figures 9.9 - 9.13) looked as if they had been torn apart rather than cleaved, in contrast to the radiolucent specimens (Figures 9.7 and 9.8) presented in the previous section. Figures 9.7 and 9.8 show the generally smooth appearance of the radiolucent samples, even the areas of deformation were smooth and rounded, not torn. Whereas in Figures 9.11 - 9.13 the torn appearance of the radiopaque cement was due to an increased flow of the matrix, particularly around the barium sulphate particles. Also evident in Figures 9.11 - 9.13 were microvoids associated with the particles of barium sulphate. Clearly these features will have an

influence on the fracture behaviour of the cement, as will be discussed later.

Figure 9.9 shows a series of scanning electron micrographs of the fracture surface of a specimen tested immediately (2 hours) after curing (WOF of 450J/m^2). The fracture surfaces of specimens tested after storage for 1 year at 21°C in air (WOF of 300J/m^2), water (WOF of 650J/m^2), Ringer's (WOF of 650J/m^2) and lipid (WOF of 450J/m^2) are shown in Figures 9.10 - 9.13 respectively. Comparing these micrographs, it was found that in general the degree of deformation on the fracture surfaces tended to be related to the WOF values for the specimens. For example, from Figures 9.11 and 9.12 it can be seen that the specimens stored in the two water based media had the roughest fracture surfaces, and they also had the highest WOF (650J/m^2). Figure 9.10 shows the micrographs for the air stored sample which had the lowest WOF (300J/m^2) and the smoothest fracture surface. The sample tested immediately after curing (Figure 9.9) and the lipid stored sample (Figure 9.13) both had WOF values of 450J/m^2, and had surface roughnesses similar to those of the two water based media, but with less deformation to the surface.

Figure 9.10 shows how smooth the fracture surface of the air stored sample was compared with the samples stored in the fluid media shown in Figures 9.11 - 9.13. The sample which was stored in air had a very planar surface with little evidence of deformation. The pre-polymerised PMMA beads from the powder component were clearly visible on the surface, indicating that they had been fractured as the crack propagated through the sample. These features gave the lower WOF sample the classical appearance of a brittle material.

The WOF of the samples stored in the fluid media were approximately twice that of the air stored sample, and Figures 9.11 - 9.13 show how much rougher the fracture surfaces were for these specimens. The fluid stored samples had much more deformed fracture surfaces with many more surface irregularities. The surfaces looked torn and

the regions where the cement had flowed and been drawn into strands were clearly obvious. There was also no evidence of the pre-polymerised beads on the fracture surfaces of the higher WOF samples, indicating that the crack had deviated around the beads and propagated solely through the matrix. The microvoids associated with the $BaSO_4$ particles were more pronounced in these samples, which had the classical appearance of a ductile material.

There were no apparent changes in the degree of deformation on the fracture surfaces with storage time in the various media, nor with storage temperature. Although the WOF increased gradually with storage in the fluid media, and decreased in air, these changes were not significant between any two consecutive time periods. Significant changes in both the WOF and the appearance of the fracture surfaces were only identified when specimens which had been stored for long-term periods (6 months and longer) were compared to those tested immediately after curing.

9.3.3 Fracture Surfaces of Fully Cured Radiopaque Cement from WOF Tests

It was found that after samples of fully cured cement had been stored in the fluid media for over 3 weeks, there was not much difference in the appearance of specimens with length of storage, nor with storage temperature. The air stored samples also showed no changes in fracture surface topography with storage time, or temperature. However, when the samples stored in air and those stored in the fluid media were compared differences in the degree of deformation on the fracture surfaces were observed.

The fracture surface of a fully cured cement sample tested immediately (2 hours) after heat treatment (WOF of 200J/m^2) is shown in Figure 9.14. Figures 9.15 - 9.18 show the fracture surfaces of samples of fully cured cement after storage at 21°C for 1 year in air (WOF of 250J/m^2), water (WOF of 620J/m^2), Ringer's (WOF of 600J/m^2) and lipid (WOF of 550J/m^2) respectively. The sample tested immediately after heat

treatment was very brittle with almost no areas of deformation on the fracture surface. The crack had taken the shortest possible route and had fractured the pre-polymerised beads as it propagated through the specimen. There was virtually no deformation associated with the particles of barium sulphate, and there were no microvoids around the particles. Comparing Figures 9.14 and 9.15, it can be seen that the fracture surface of the sample which had been stored in air at 21°C for 1 year was slightly more deformed than the sample tested immediately after heat treatment. The air stored sample also had a slightly higher WOF than the sample tested immediately after heat treatment, 250J/m^2 as opposed to 200 J/m^2, indicating that with storage in air at 21°C the cement became a little more ductile. This was possibly due to the ingress of small amounts of water vapour from the atmosphere during storage.

Despite the slight variation in WOF (550J/m^2 - 620J/m^2) for samples stored in the three fluid media, the fracture surfaces were all very similar, see Figures 9.16 - 9.18. Although some of the pre-polymerised beads had been fractured, all three surfaces had experienced plastic deformation, and in general the crack had tended to deviated around the beads. There was also deformation associated with the barium sulphate, microvoids had been formed around the particles and the matrix between them had been torn apart. It appeared, with the fully cured cement, that the deformation associated with long-term storage in the fluid media was not as dependant on WOF value, nor the specific storage condition, as for specimens of normal cement.

9.3.3.1 Examination of Fracture Surfaces to Establish Depth of Ductile Region

When fully cured specimens which had been stored in the fluid media for short periods (1 - 3 weeks) were examined it was found that the fracture surfaces exhibited both a planar brittle region and a deformed ductile region. It was also found that there were no differences between the appearance of samples stored in any of the fluid media. Figures 9.19 - 9.22 show the fracture surfaces of fully cured cement samples after storage in water at 21°C for 1 week (WOF of 300J/m^2), at 37°C for 1 week

(WOF of 410J/m^2), at 21°C for 3 weeks (WOF of 413J/m^2), and at 37°C for 3 weeks (WOF of 442J/m^2) respectively. These figures show that the crack propagated initially in a brittle manner, fracturing the pre-polymerised beads as it progressed through the sample. Towards the end of the crack, as it approached the far edge of the specimen (the base of the triangle), the crack began to deviate around the beads leading to a deformed region of ductile failure. The width of the ductile region appeared to be related to the length and temperature of storage in the fluid media, rather than to the WOF values.

From Figure 9.19 it can be seen that the sample stored for 1 week in fluid at 21°C had a ductile region which was approximately 500 micrometers deep. The fracture surface of a sample which was stored in fluid at 37°C for 1 week, and had a ductile region approximately 800 micrometers wide, is shown in Figure 9.20. Figure 9.21 shows a sample which was stored in fluid for 3 weeks at 21°C, and had a ductile region approximately 1000 micrometers wide. Once samples had been stored in fluid at 37°C for 3 weeks or longer, or in fluid at 21°C for longer than 3 weeks, the entire fracture surface failed in a ductile manner, as shown in Figure 9.22. The mean depth of the ductile region and the mean WOF for these short-term storage samples are summarised in Table 9.1.

The apparent texture on the surface of the sample shown in Figure 9.19 was an artefact caused by damage to the polymer surface by the electron beam (as reported previously by Cameron, Mills, Jackson and Macnab, 1974), and was not deformation sustained during the fracture process.

9.3.4 Fracture Surfaces of Normal Radiopaque Cement from Rapid Fracture Tests

Figures 9.23 and 9.24 show the fracture surfaces produced from rapid fracture tests for samples stored for 1 week in air at 21°C (WOF of 752J/m^2) and for 12 weeks in water at 21°C (WOF of 736J/m^2) respectively. From these figures it can be seen that the rapid fracture surfaces tended to be smoother than when the crack growth was controlled (i.e. in the Tattersall-Tappin WOF tests). Also there did not appear to be any microvoids associated with the $BaSO_4$ on the surfaces of the rapid fracture specimens.

Although no significant differences in the WOF values from the rapid fracture tests for samples stored in the different environments were identified (see section 5.1.2), scanning electron microscopy of the fracture surfaces showed that specimens stored in the fluid media had rougher, more deformed surfaces than those stored in air. From Figure 9.23 it can be seen that the fracture surface of the air stored sample was very smooth with little evidence of any deformation. The pre-polymerised beads were clearly visible on the surface of the specimen, indicating that the crack had propagated through the beads as well as the matrix of the cement. The fracture surface of the water stored sample shown in Figure 9.24 was much rougher than the sample stored in air, with many more surface irregularities and areas of deformation. Although there was evidence of the pre-polymerised beads on the surface, it was apparent that the crack had propagated through some of the beads and deviated around others. This implied that the ingress of the water still had a plasticising effect on these specimens even though this was not reflected in the WOF results.

9.4 Discussion of Microscopy

9.4.1 Cement Powder

The scanning electron micrographs obtained for Simplex P radiopaque cement were very similar to those obtained by other workers (Kusy, 1978, and Brauer, Termini and Dickson, 1977), and showed a fraction of a fine powder mixed with much larger spherical beads. Brauer, Termini and Dickson (1977) found that the powders of both radiopaque and radiolucent cement contained spherical beads of an average size of 30μm, and a fine powder which tended to aggregate into clusters of particles which were between 1 and 100μm in size. No significant difference between the bead size distributions of radiopaque and radiolucent powder was observed by the authors, nor could they distinguish between the fine powders of the two cement types. It was therefore concluded that the fine powder consisted of very small PMMA particles, which in the radiopaque cement were also mixed with barium sulphate particles. This is consistent with our findings on the composition of Simplex bone cement powder.

Various different sizes for the pre-polymerised PMMA beads have been reported and these are summarised in Table 9.2. From this table it can be seen that there is a great variation in the reported size distributions for acrylic bone cements and dental resins. This has been attributed to differences between the size distributions of the many brands of cement which are currently on the market.

The size of the barium sulphate particles was reported to range from 0.1μm - 3.8μm with the majority around 1μm (Davies, 1989), which compares well with our observation that the fine powder of Simplex cement consists of approximately micron sized particles.

The effect of the features on the fracture behaviour of the cement will be discussed in section 9.4.3.1.

9.4.2 Cured Cement

The composite nature of self-curing acrylic bone cement was clearly evident from the optical micrographs shown in Figures 9.4 and 9.5, and has also been observed by Smith (1961), Kusy (1978), Kusy, Mahan and Turner (1976), and Cameron, Mills, Jackson and Macnab (1974). The latter group suggested that the spheres observed on the surface of the cured cement were the pre-polymerised beads of the initial powder component.

Smith (1961) suggested several reasons why the pre-polymerised beads remained in the cured material. These included i) differences in composition between the bead and the matrix, ii) differences in molecular weight between the bead and the matrix, iii) the formation of a "skin" on the surface of the bead, and iv) the formation of stress concentrations around the beads due to localised shrinkage during polymerisation. Kusy (1978) also suggested that residual stresses due to differential compositions, and differential curing and cooling rates between the beads and the matrix would lead to the retention of the bead-matrix interface. We also suggest that the working time of the cement is relatively short, approximately 8 minutes depending on the brand of cement and the mixing conditions, so there would probably be insufficient time for the residual monomer to dissolve the larger beads, and that it is only their surface which is attacked, as also suggested by Kusy and Turner (1974). These authors showed that the average size of the beads in the powder component tended to be smaller than those in the cured cement, and that the volume fraction of beads in the powder was greater than that in the cured cement. It was therefore concluded that the monomer completely dissolved the smaller beads to produce the matrix phase, and that only the outer surface of the larger beads was dissolved.

It is the heterogeneous structure of bone cement which distinguishes it from industrial PMMA, and (along with the relatively high porosity and residual monomer contents) accounts for some of the observed differences in the mechanical properties of the two

materials (see section 2.6). Smith (1958) has shown that fracture behaviour of the two materials can be related to the different microstructures, and that the two materials do not behave in the same manner.

9.4.2.1 Porosity Content of the Cured Cement

Kusy, Mahan and Turner (1976) showed evidence of porosity actually within the pre-polymerised beads, and suggested that the matrix porosity was an artifact from the polishing preparatory technique. However, the results of our study indicate that although the polishing technique may introduce additional porosity, there is an inherent inter-bead porosity, as revealed on the fracture surfaces of our WOF specimens (see Figures 9.7 - 9.24). As discussed in section 9.2, this porosity was thought to be due to either the entrapment of air during mixing or to the evaporation of pockets of trapped monomer during curing. It has been suggested that the numerous small spherical pores observed in the cement are due to evaporation of pockets of trapped monomer, and that the larger irregularly shaped pores are due to air entrapment (Lautenschlager, Stupp and Keller, 1984).

Many different values for the porosity content of bone cements have been reported in the literature, and these are summarised in Table 9.3. Black (1988) suggested that this variability in the porosity content of bone cement was due, mainly, to different mixing techniques.

There was no porosity associated with the particles of barium sulphate in polished sections of the radiopaque cement, an observation which was also noted by Kusy (1978). This would suggest that the microvoids which were associated with the barium sulphate on the fracture surfaces formed as a direct result of the fracture processes occurring within the cement. This will be discussed in more detail in section 9.4.3.1.

9.4.3 Fracture Surfaces of Normal Cement Samples

Several authors (Black, 1988, Kusy, 1978, and Smith, 1961) have suggested that the interface between the prepolymerised beads and the recently polymerised matrix is a source of weakness in bone cement. Kusy (1978) suggested that inter-bead failure was an indication of poor adhesion between the beads and the matrix and that even when trans-bead failure occurred the bead-matrix interface could act as a source for secondary crack propagation. However, Kusy, Mahan and Turner (1976) showed that two-phase dental acrylics were more brittle than industrial PMMA, they found that the bead-matrix interface was not a source of weakness, and that their material, in cleavage tests, failed by fracture of the prepolymerised beads which the authors termed "transgranular cleavage". The authors also concluded that the matrix was more brittle than the beads, and that occasionally the beads acted as "crack stoppers". In our study, where controlled crack growth was achieved, it was found that on the whole the crack tended to deviate around the beads and propagate solely through the matrix. There was however also evidence of cleavage of the PMMA beads in the more brittle samples.

The smoother fracture surfaces, shown in Figures 9.7, 9.10, 9.14 and 9.15 revealed evidence of the pre-polymerised beads beneath the surface. It appeared that these beads had actually been cleaved as the crack propagated through the sample. With the high WOF samples, shown in Figures 9.11, 9.12 and 9.16, this feature was lost due to the rougher, more deformed fracture surface. Work done by Topoleski, Ducheyne, and Cuckler (1991) on the fractography of rapid, fatigue, and slow crack growth specimens showed evidence of "microcraze shower" formation. This occurred where the molecular weight of the PMMA was too low to form fibrils or craze across the damaged zone around the crack tip (see Figure 9.25). The authors wrote that "the microcraze shower forms the damage zone ahead of the crack tip ..... As energy is added to the system, the microcrazes are connected, and the crack extends ..... The characteristic irregular fatigue surface morphology may be the product of the

microcraze coalescence. The smooth, rapid fracture surface ..... indicates that no microcraze damage zone was formed." The authors also suggested that "the material rupture within the microcraze shower probably occurs preferentially through the binding phase PMMA." It has also been reported by Black (1988) that extreme levels of absorption can lead to excessive local swelling and hence induce the formation of crazes within the polymer. It is therefore suggested here, that in the rougher samples the crack path actually deviated around the beads and propagated solely through the recently polymerised PMMA matrix, whereas in the more brittle samples the crack propagated through both the bead and the matrix.

As discussed in section 9.3.2, higher WOF samples tended to have rougher fracture surfaces, with more surface irregularities, and an increased flow of cement. The microvoids associated with the particles of barium sulphate were also more pronounced in the higher WOF samples. In the lower WOF samples the pre-polymerised beads of the powder component were clearly visible. From the fracture surfaces it appeared that different fracture mechanisms were operating in the high and low WOF samples. One where the crack propagates through both the bead and the matrix leading to a flat planar surface classic of a brittle material. The other where the crack deviates around the bead and propagates solely through the matrix producing a highly deformed surface classic of a ductile material.

These differences in the fracture surfaces may indicate that ingress of the fluids into the cement preferentially attacked the matrix, weakening the binding phase rather than the bead, thus encouraging the crack to deviate around the beads. Alternatively the fluids may have attacked the interface between the bead and the matrix, also encouraging the crack to deviate around the beads, and hence creating an easier but longer crack path. When the sample which was tested immediately after curing was examined, however, it too had failed in a ductile manner, i.e. the crack had deviated

around the bead. This could have been due to moisture within the cement when it first set, which dried out as the sample was aged in air.

James, Jasty, Davies, Piehler and Harris (1992) showed that fatigue cracks in their bone cement samples initiated at internal pores and travelled outwards towards the edge of the specimens. This was characterised by "river patterns" which ran in the direction of crack propagation. The micrographs of James *et al*'s (1992) fatigue tested specimens had a similar appearance to the specimens tested in this study (see Figures 5.19 - 5.21). Our WOF samples also showed river patterns emanating from internal pores, indicating a similar failure mechanism to that observed with the fatigue specimens. Topoleski, Ducheyne and Cuckler (1990) also found that the fracture surface of slow continuous crack growth specimens was identical to those of fatigue crack growth specimens, and their micrographs of fatigue specimens are also similar to our WOF samples. This would indicate that the same microstructural failure mechanisms are occurring in both our controlled crack growth tests and in fatigue tests. Thus any treatments which affect the failure mechanisms of our WOF specimens are also likely to influence the failure mechanisms of the cement *in vivo*.

It is obvious from the microscopy of the fracture surfaces that the observed changes in the WOF values were due largely to changes in crack length and true surface area, as opposed to the apparent or geometric surface area (that which was measured to calculate the WOF). The rougher the fracture surface, the longer the crack length and the greater the true surface area. Since it was the geometric area which was used to calculate the WOF, an artificially high WOF value was obtained. It is postulated that if the true surface areas had been used to calculate the WOF, then few changes in the WOF with storage condition would have been observed. However, since the increase in crack length increases the fracture energy and hence also increases the resistance to crack growth, it was valid to use the geometric area to calculate the WOF when comparing different treatments on the fracture behaviour of a single material.

9.4.3.1 Effect of Barium Sulphate on the Fractography

Microvoids were clearly evident around the particles of barium sulphate as seen in Figures 9.11 - 9.13. These features introduce additional defects into the cement structure and will therefore have an influence on the fracture behaviour of the cement, as discussed in section 2.7. It has been postulated by Owen and Beaumont (1980), Beaumont (1977), and Beaumont (1979) that the microvoids are formed by the opening up of cavities around each weakly bonded barium sulphate particle. As also discussed in section 2.7, the above authors suggested that the crack then propagated through the cement by the linking up of these voids. It was suggested by Beaumont (1977) that the coalescence of the voids occurred first by their elongation then by tearing of the recently polymerised PMMA matrix between them. The micrographs shown in Figures 9.11 - 9.13 would support this theory.

9.4.4 Fracture Surfaces of Fully Cured Cement Samples

As discussed in section 9.3.3, the sample which had been stored in air at 21°C for one year was rougher and had a slightly higher WOF than the sample which was tested immediately after heat treatment. It was suggested that this was as result of the ingress of small amounts of water vapour from the atmosphere during storage. This theory is supported by the weight change results, which showed that samples of fully cured cement experienced a slight weight gain with storage time in air (see section 6.1.3).

It was also found, in section 9.3.3, that there were no differences in the fractography of samples which had been stored in any of the three different fluid media. Nor were there any differences in the fractography of samples stored at the two temperatures. As discussed in section 4.2.2, this has been attributed to the elimination of the residual monomer as a variable from within the cement. The main differences in the WOF of normal samples which were stored in the different media and at the two temperatures were due to variations in the leaching of the monomer from the cement. Since the residual monomer content of the fully cured cement did not change with storage, the

WOF was similar for all three fluids and both temperatures. As the fractography of the cement is related to the WOF, then it was unlikely that any variations in the fractography would be observed either.

Once the fully cured cement had been stored in the fluid media for over 3 weeks, no variation in the fractography was observed with longer storage periods. This can again be related to observations about the WOF. It was shown in section 4.1.3 that the most dramatic changes in the WOF of the fully cured cement occur within the first few weeks of storage (within 3 months). Hence one would expect that the most significant changes in the fractography of the cement would also occur within this time period.

9.4.4.1 Depth of Ductile Regions

It was shown in section 9.3.3.1 that samples of fully cured cement which were stored in the fluid media for 1 and 3 weeks exhibited mixed mode failure. Whilst the bulk of the sample failed in a brittle manner, the end of the crack (back of the triangle) failed in a ductile manner. It was found that the width of this ductile region appeared to be dependent upon the length and temperature of storage. Since the amount of environmental ingress into the cement was also found to be dependent upon the length and temperature of storage in the fluid media (see section 6.3.3) it was thought that the ductile region on these fracture surfaces was a result of the ingress of the fluid media. It is postulated that the width of the ductile regions shown in Figures 9.19 - 9.22 is related to the depth of environmental ingress into the cement.

9.4.5 Rapid Fracture Surfaces

From the fractography of the rapid fracture specimens, it can be seen that the storage fluids did have a plasticising effect on the cement, even though this was not evident from the WOF value obtained with the rapid fracture tests. Although all the samples fractured in a brittle manner, those which had been stored in the fluid environments for 3 months did show some features which indicated a degree of plastic deformation.

Huggett, Bates and Packham (1987) have reported that when acrylic dental resins are tested in impact loading they fail in a brittle manner, which supports our observations of the failure mode of bone cement under rapid fracture test conditions.

The more brittle rapid fracture surfaces, shown in Figure 9.23, had a similar appearance to those shown by Lamb, Ellis and van Noort (1985). The area where the crack initiated was relatively rough compared to the central region of the fracture surface, which was almost featureless. The area at the back of the specimen where the crack terminated was striated, the striations running parallel to the direction of crack propagation. Lamb, Ellis and van Noort (1985) reported that these fracture surface features were typical of Charpy tests specimens.

There did not appear to be any microvoids associated with the $BaSO_4$ on the surfaces of the rapid fracture specimens, indicating that the crack had not propagated by void coalescence as it had in the controlled crack growth (Tattersall-Tappin) tests.

9.5 Summary of Microscopy

It has been shown that storage of samples of both normal and fully cured cement in the fluid media resulted in ductile failure, whereas storage of the samples in air tended to result in brittle failure. The brittle failure mode was associated with cleavage of the pre-polymerised beads and virtually no de-bonding of the matrix and the barium sulphate. Ductile failure was associated with crack propagation solely through the matrix phase as the crack deviated around the pre-polymerised beads. Also evident on the specimens which failed in a ductile manner, were microvoids associated with the barium sulphate. The major effect of these two energy absorbing processes was to increase the WOF of the samples of cement.

It has been postulated that since the fracture surfaces of our WOF samples are almost identical to fatigue fracture surfaces obtained by other workers, the microstructural failure mechanisms are similar in both samples. Thus any treatment which influences the failure mechanisms of our samples will also be relevant to the *in vivo* failure of bone cement.

Table 9.1 : Correlation of WOF Values and Depth of Ductile Region on Fully Cured Cement Samples

Storage Condition	Number of Samples	95%CI WOF	95%CI Depth
1 week fluid 21°C	3	267±72	433±72
1 week fluid 37°C	4	382±40	950±113
3 weeks fluid 21°C	9	412±23	867±94
3 weeks fluid 37°C	5	458±14	complete

NOTES

i) WOF is in J/m^2

ii) Ductile region depths are in μm.

Table 9.2 Reported Sizes for the Pre-polymerised PMMA Beads

Author	Reported Size
Smith (1961)*	0.5% greater than 353μm 8-19% range from 152 to 353μm 75% range from 75 to 152μm 3-12% range from 53 to 75μm 1-8% less than 53μm
Kusy and Turner (1974)*	average size less than 20μm maximum size 160μm
Brauer *et al* (1977)	average size 30μm
Kusy (1978)	average size 80μm
Lautenschlager *et al* (1984)	range from 30 to 150μm
Black (1988)	range from 10 to 30μm
Davies (1989)	maximum 2.5% range from 75 to 125μm minimum 65% range from 53 to 75μm minimum 25% less than 53μm
This study	range from 10 to 100μm

* Figures for acrylic dental resins not bone cements.

Table 9.3 Reported Values for Porosity Content of Bone Cement

Author	Reported Porosity Content
Bayne *et al* (1975)	11%
Haas *et al* (1975)	1 - 10%
Kusy (1978)	5 ± 4%
Noble (1983)	5 - 15%
Lautenschlager *et al* (1984)	8%
Black (1988)	1 - 10%

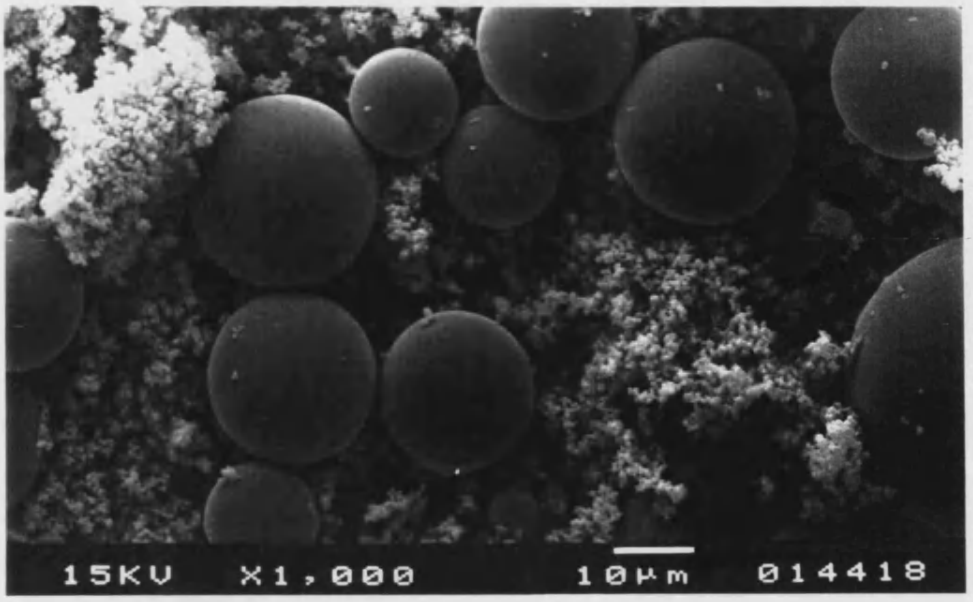


Figure 9.1a : Scanning Electron Micrograph of Simplex P Radiopaque Bone Cement Powder - Magnification x1000.

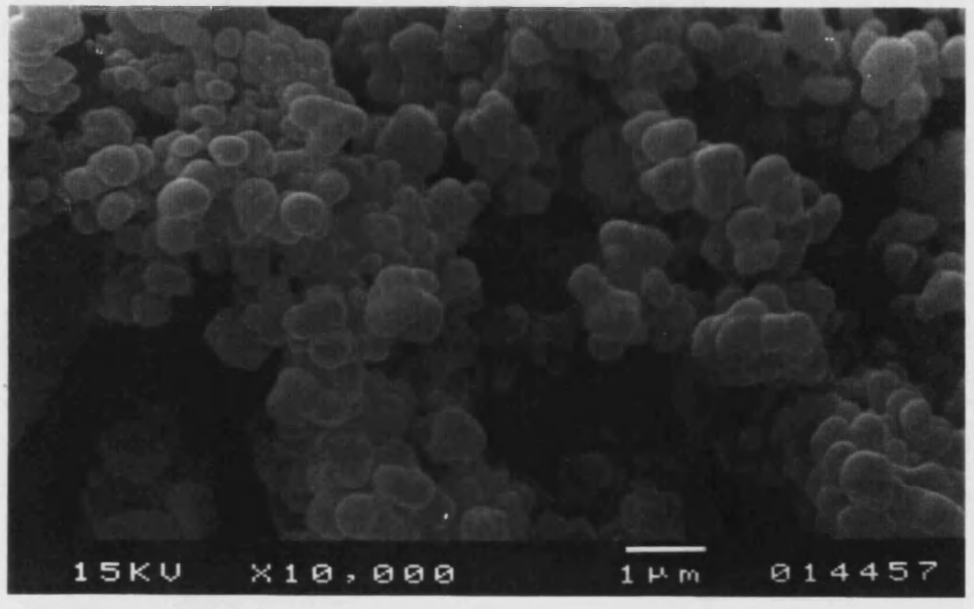


Figure 9.1b : Scanning Electron Micrograph of Simplex P Radiopaque Bone Cement Powder - Magnification x10 000.

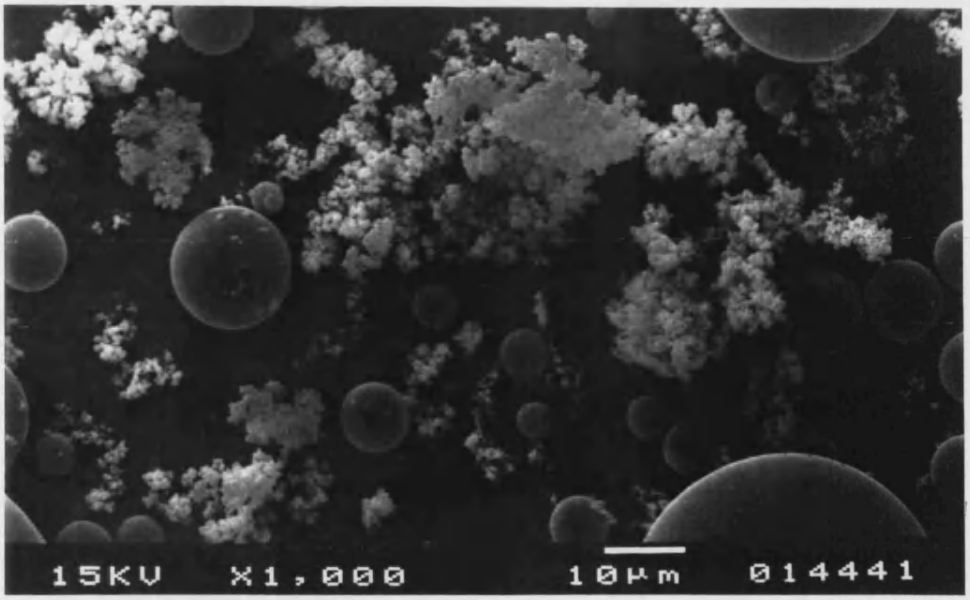


Figure 9.2a : Scanning Electron Micrograph of Simplex P Radiolucent Bone Cement Powder - Magnification x1000.

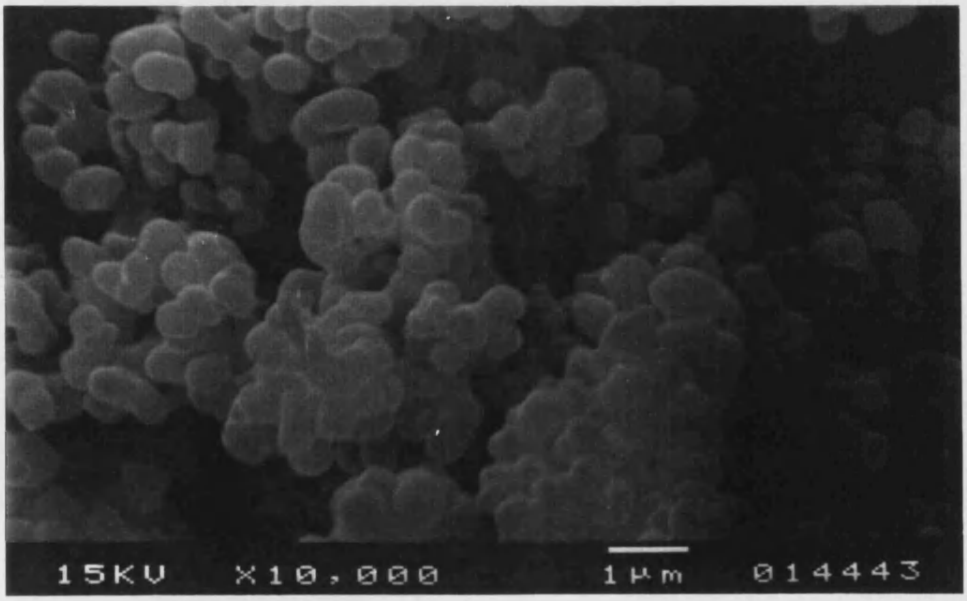


Figure 9.2b : Scanning Electron Micrograph of Simplex P Radiolucent Bone Cement Powder - Magnification x10 000.

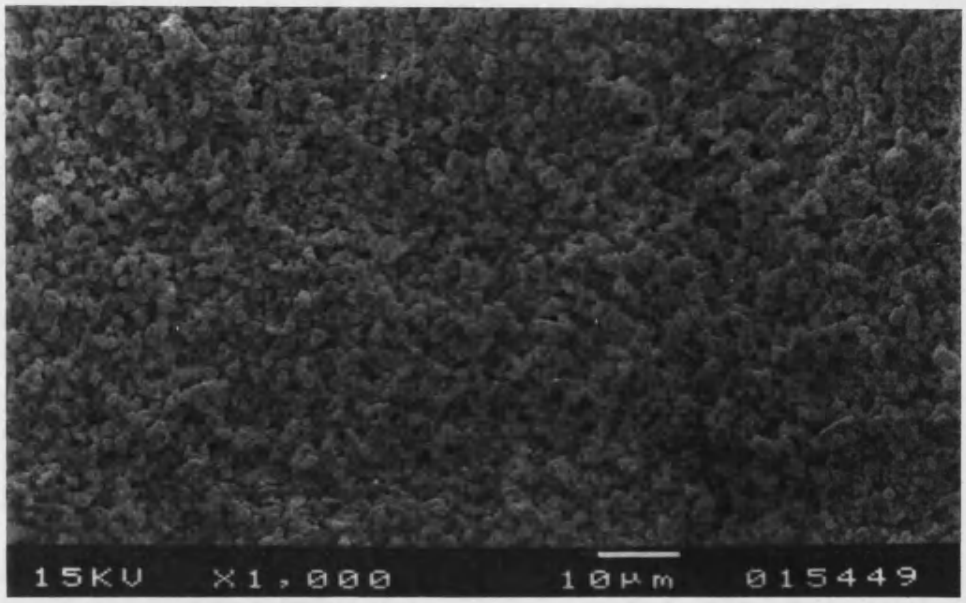


Figure 9.3a : Scanning Electron Micrograph of Simplex P Barium Sulphate Powder - Magnification x1000.

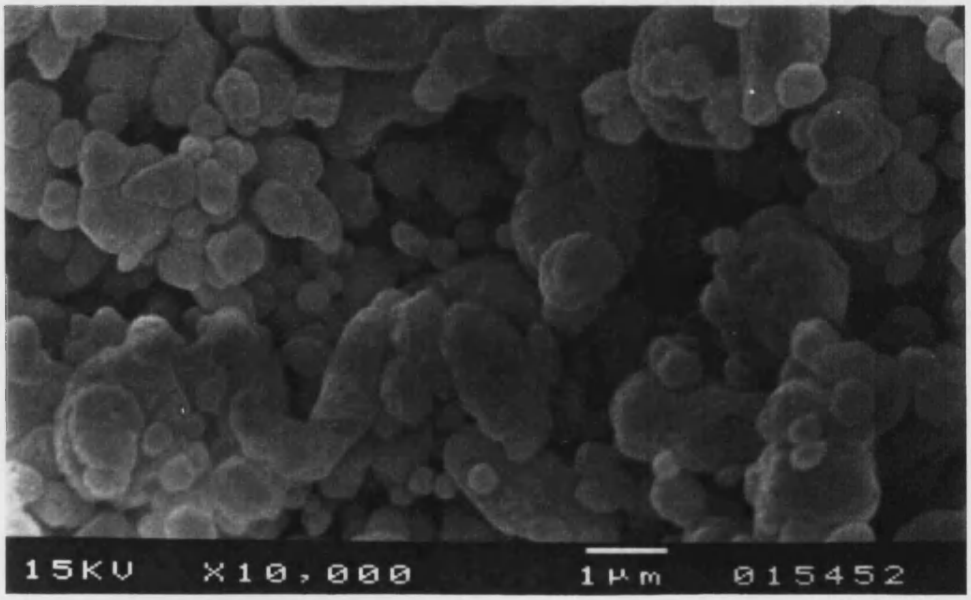


Figure 9.3b : Scanning Electron Micrograph of Simplex P Barium Sulphate Powder - Magnification x10 000.

Figure 9.4a : Optical Micrograph of a Polished Section of Simplex P Radiopaque Bone Cement - Magnification x80.

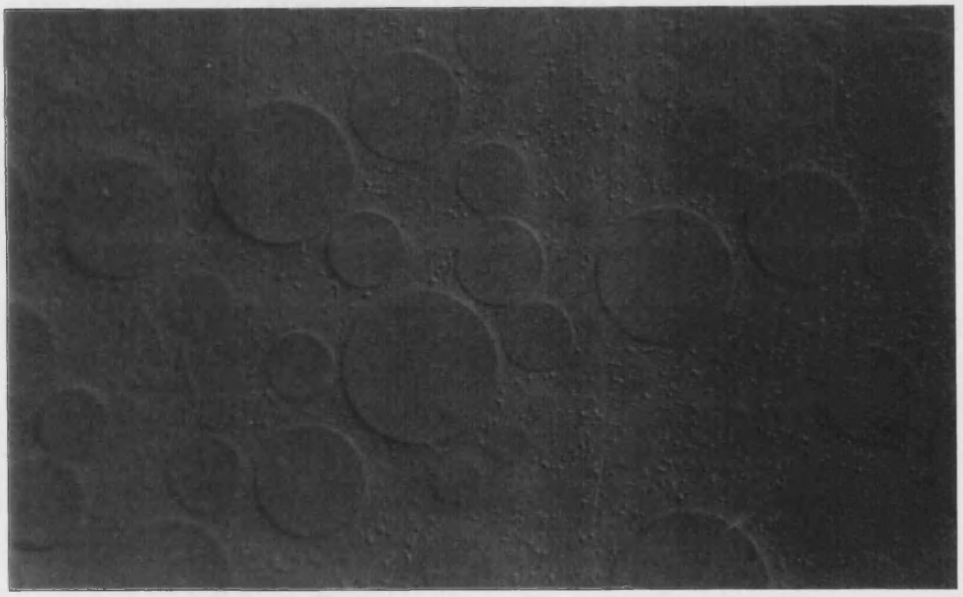


Figure 9.4b : Optical Micrograph of a Polished Section of Simplex P Radiopaque Bone Cement - Magnification x200.

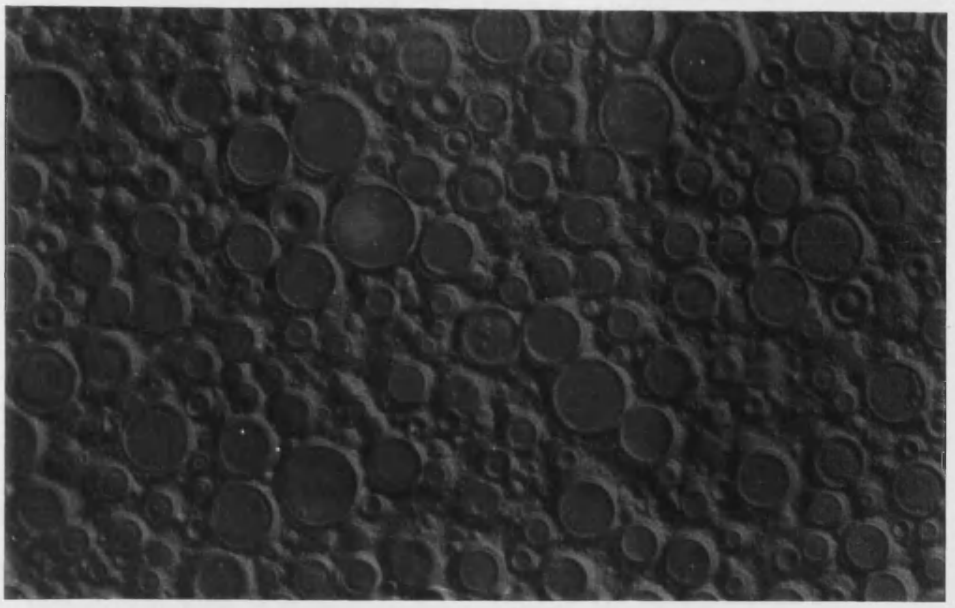


Figure 9.5a : Optical Micrograph of a Polished Section of Simplex P Radiolucent Bone Cement - Magnification x80.

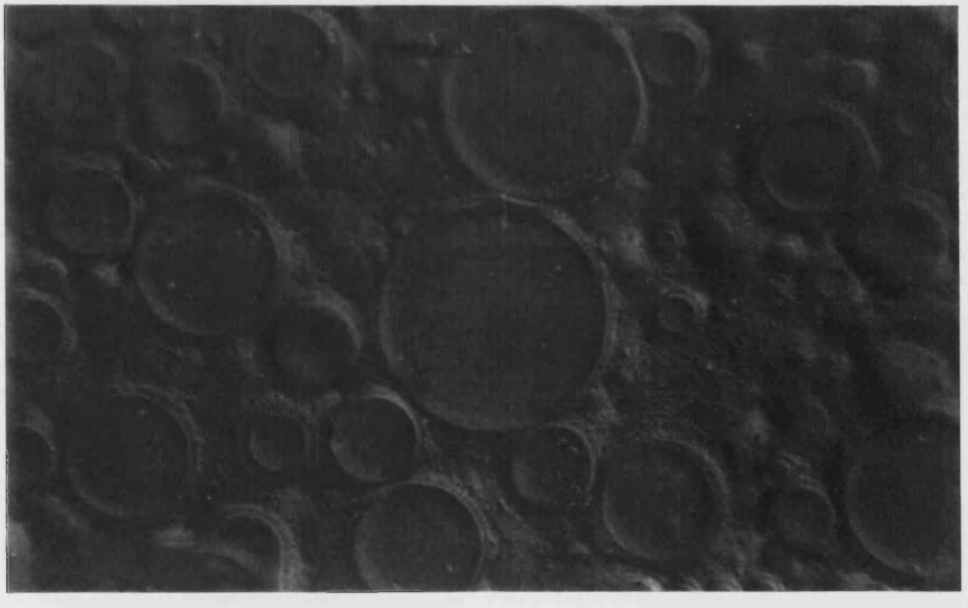


Figure 9.5b : Optical Micrograph of a Polished Section of Simplex P Radiolucent Bone Cement - Magnification x200.

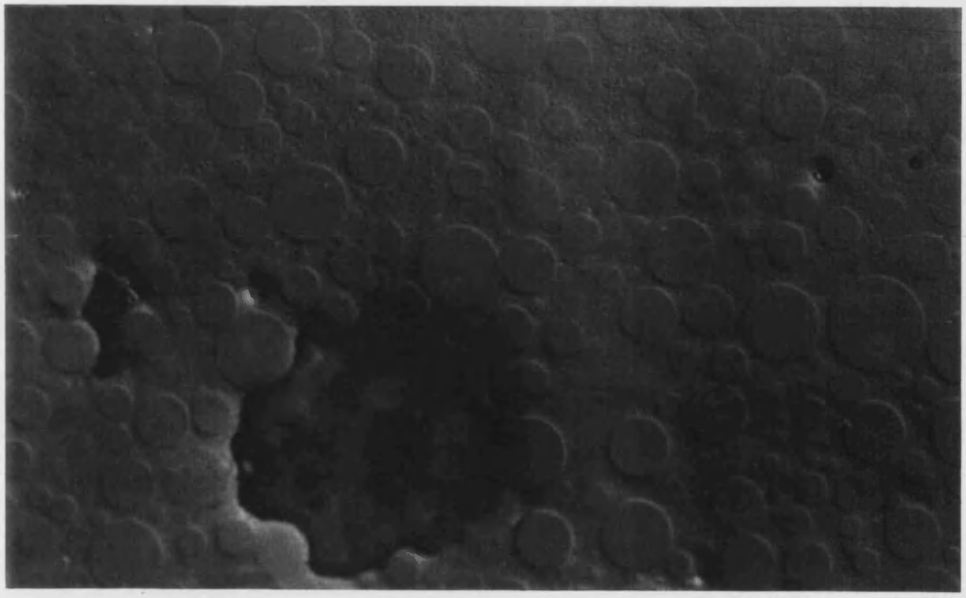


Figure 9.6a : Optical Micrograph of Porosity in a Polished Section of Simplex P Radiopaque Bone Cement - Magnification x80.

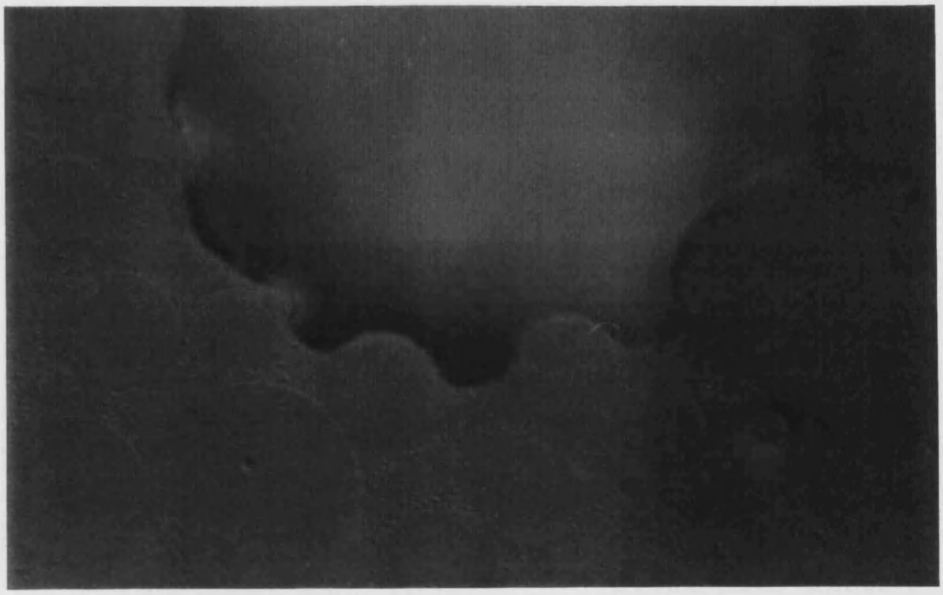


Figure 9.6b : Optical Micrograph of Porosity in a Polished Section of Simplex P Radiopaque Bone Cement - Magnification x200.

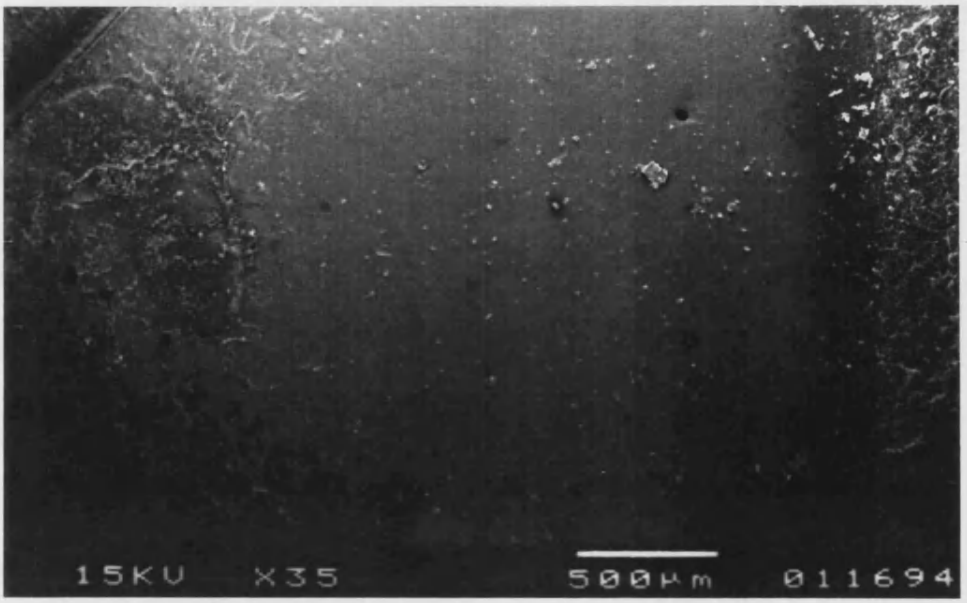


Figure 9.7a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiolucent Cement After Storage in Water at 37°C for 1 Week - Magnification x35.

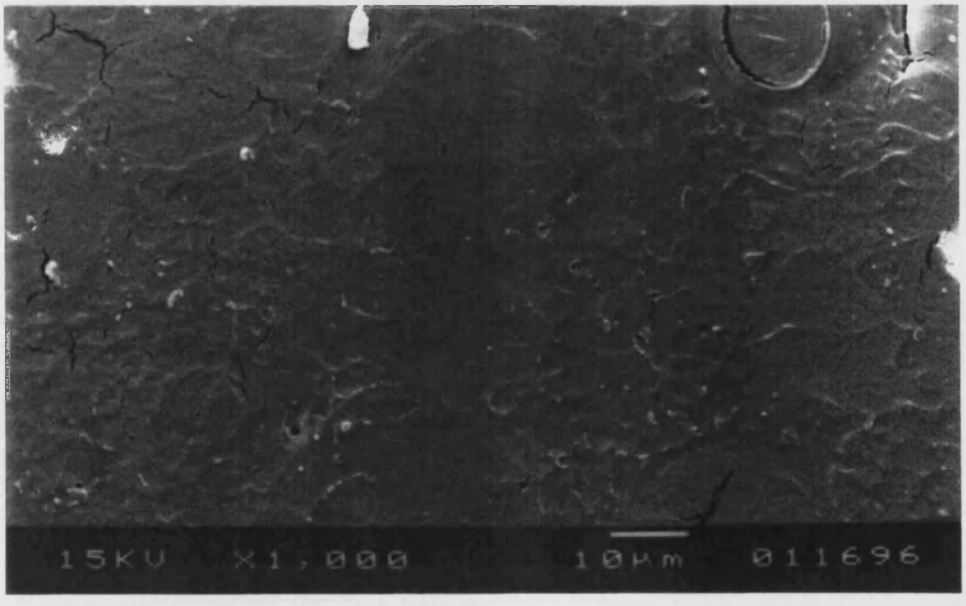


Figure 9.7b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiolucent Cement After Storage in Water at 37°C for 1 Week - Magnification x1000.

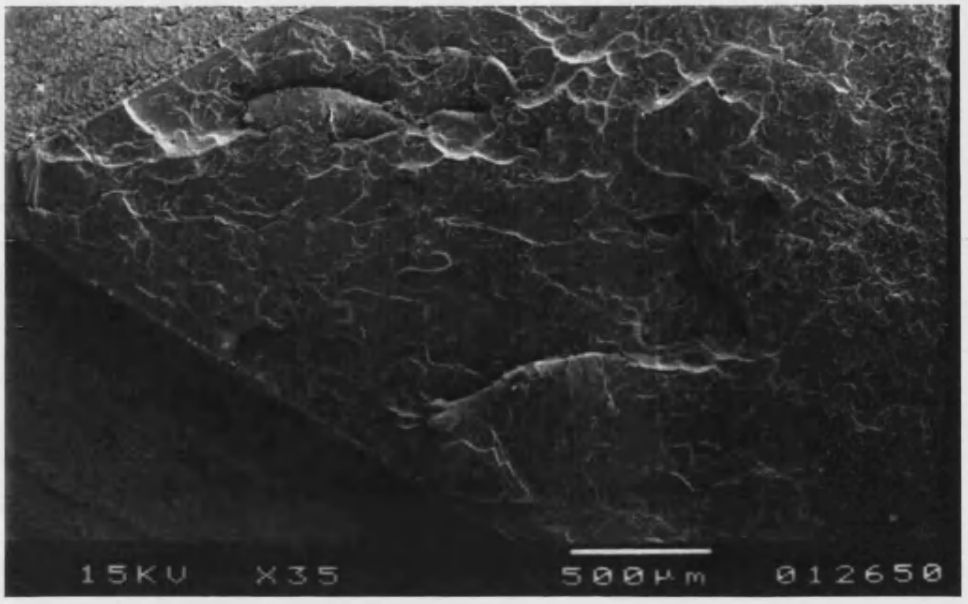


Figure 9.8a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiolucent Cement After Storage in Water at 21°C for 1 Week - Magnification x35.

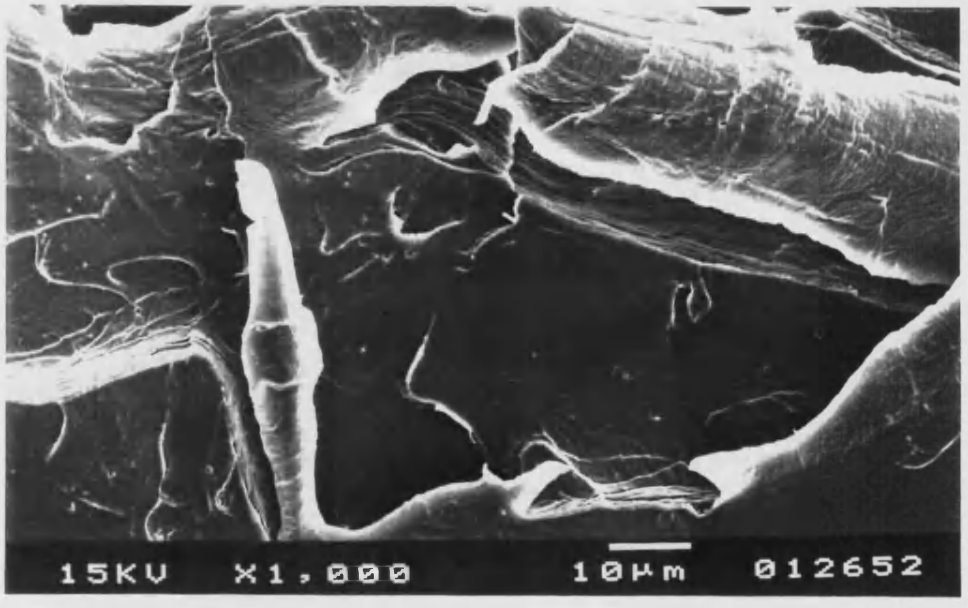


Figure 9.8b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiolucent Cement After Storage in Water at 21°C for 1 Week - Magnification x1000.

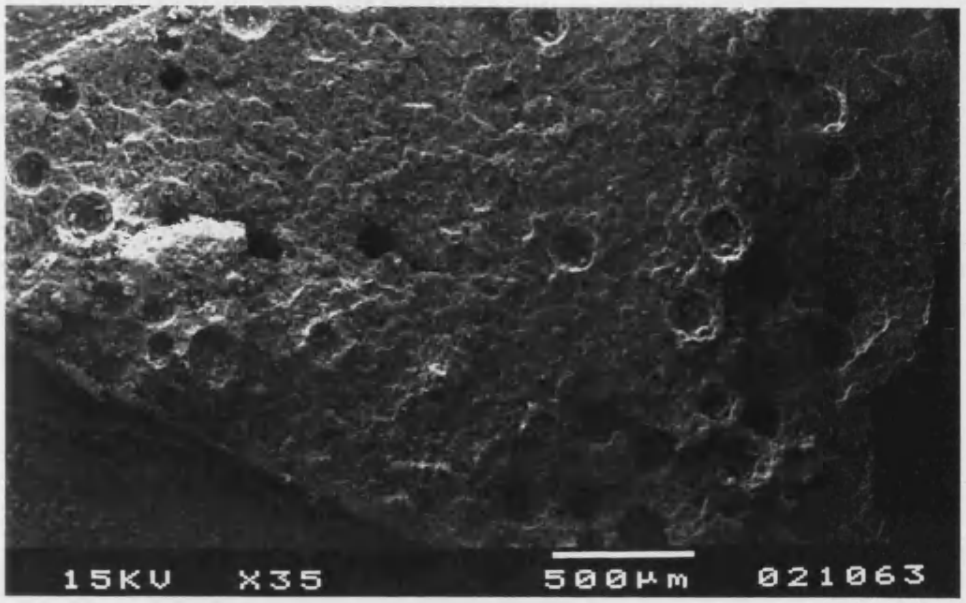


Figure 9.9a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement Tested Immediately (2 hours) After Curing - Magnification x35.

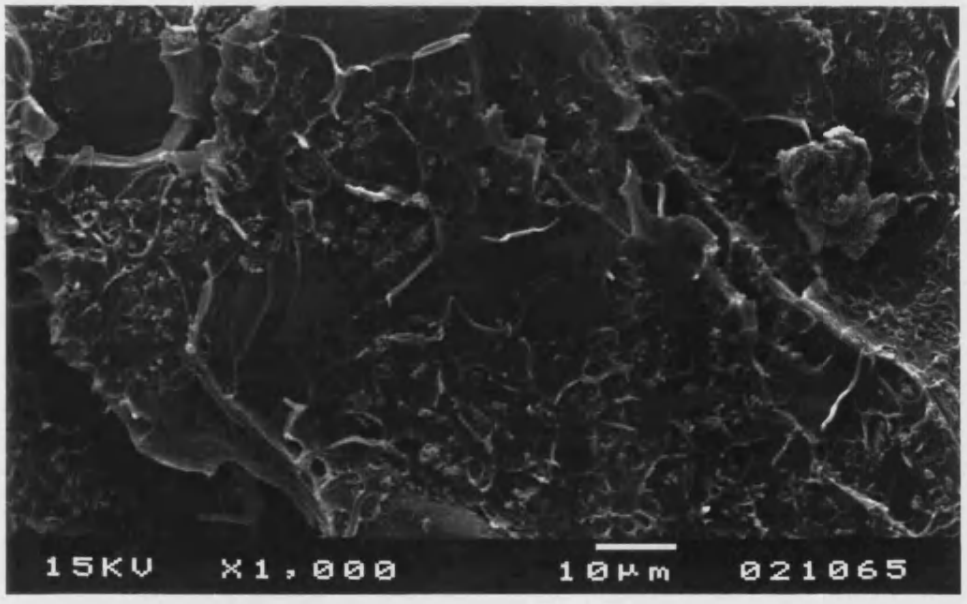


Figure 9.9b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement Tested Immediately (2 hours) After Curing - Magnification x1000.

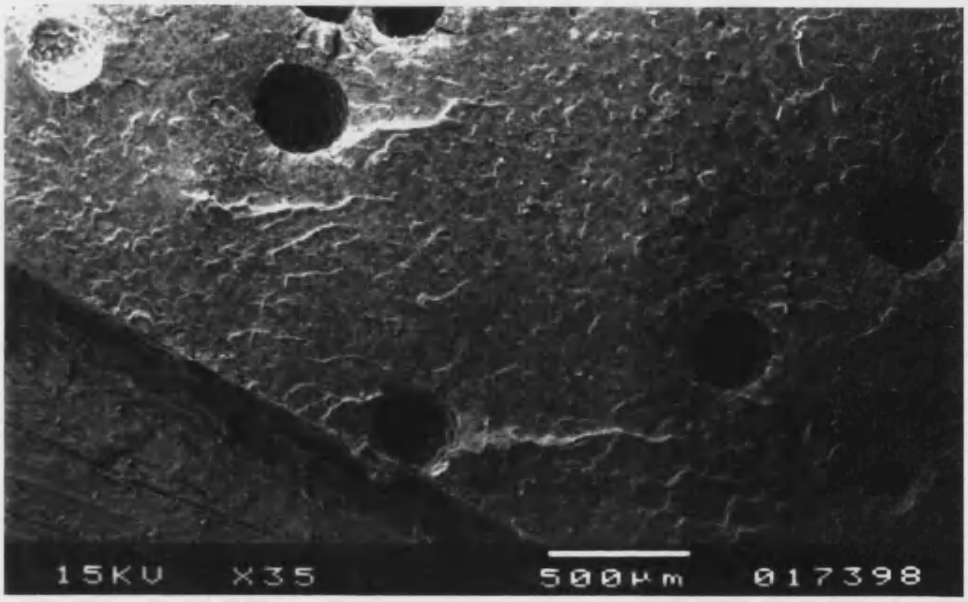


Figure 9.10a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Air at 21°C for 1 Year - Magnification x35.

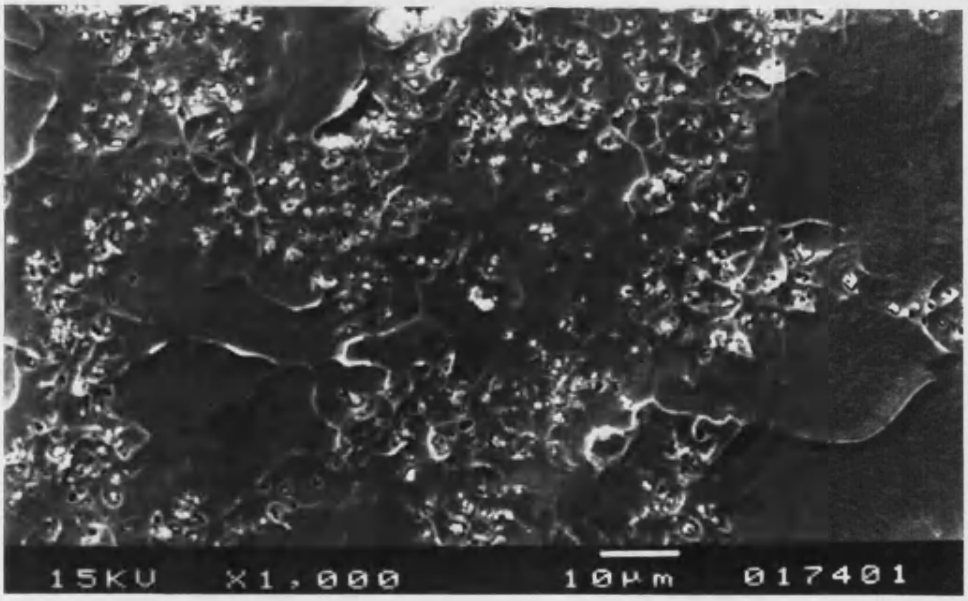


Figure 9.10b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Air at 21°C for 1 Year - Magnification x1000.

Figure 9.11a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Water at 21°C for 1 Year - Magnification x35.

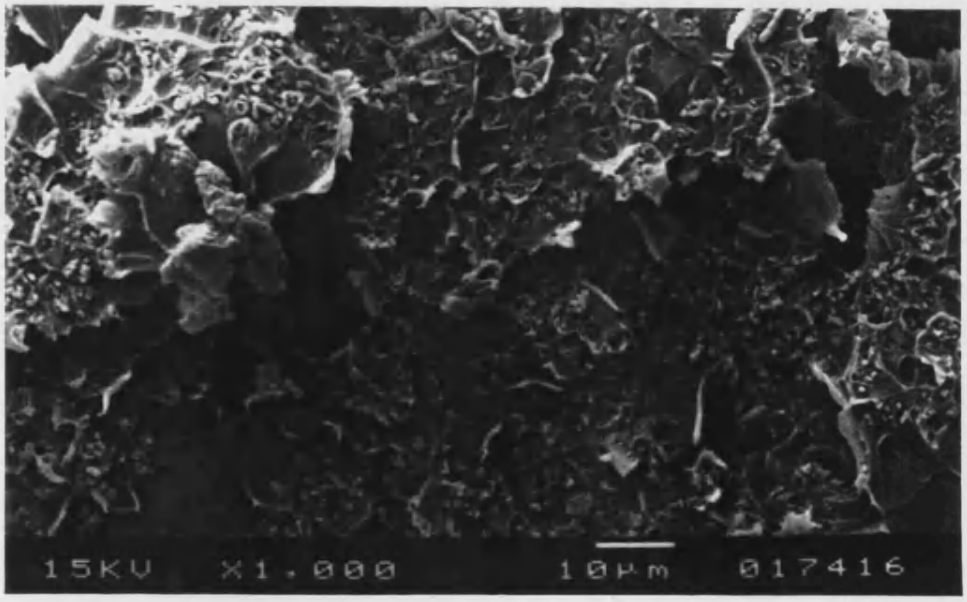


Figure 9.11b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Water at 21°C for 1 Year - Magnification x1000.

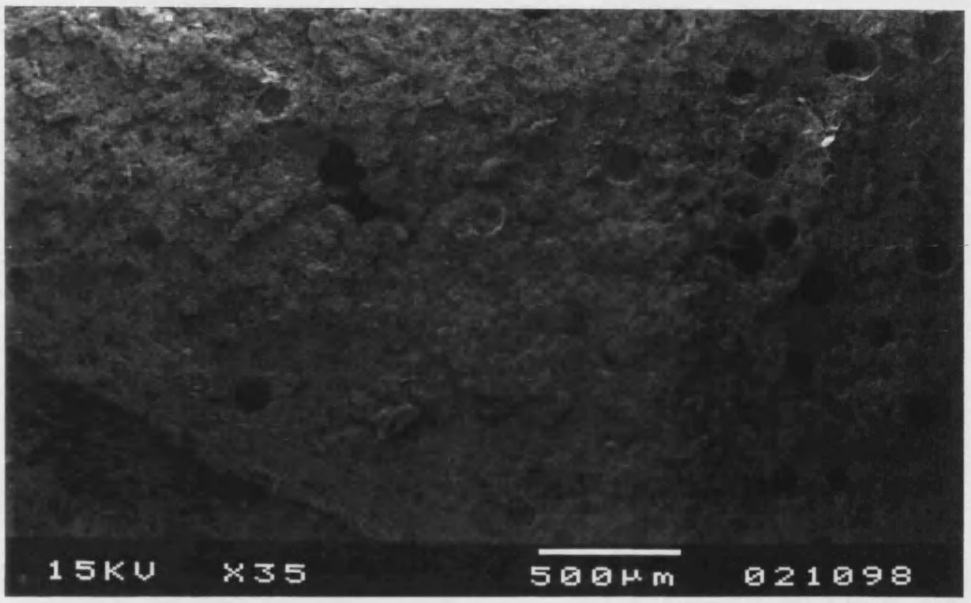


Figure 9.12a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Ringer's at 21°C for 1 Year - Magnification x35.

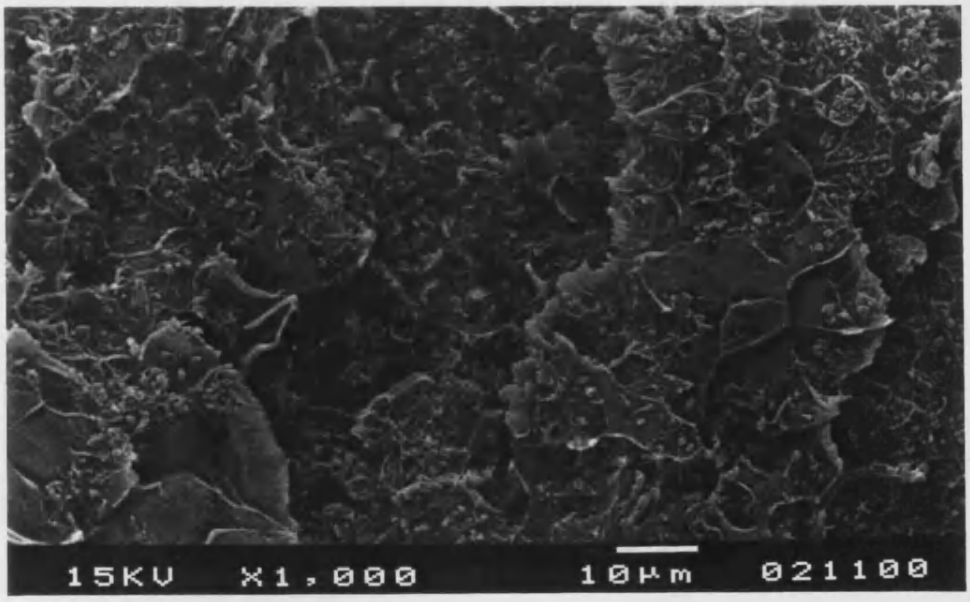


Figure 9.12b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Ringer's at 21°C for 1 Year - Magnification x1000.

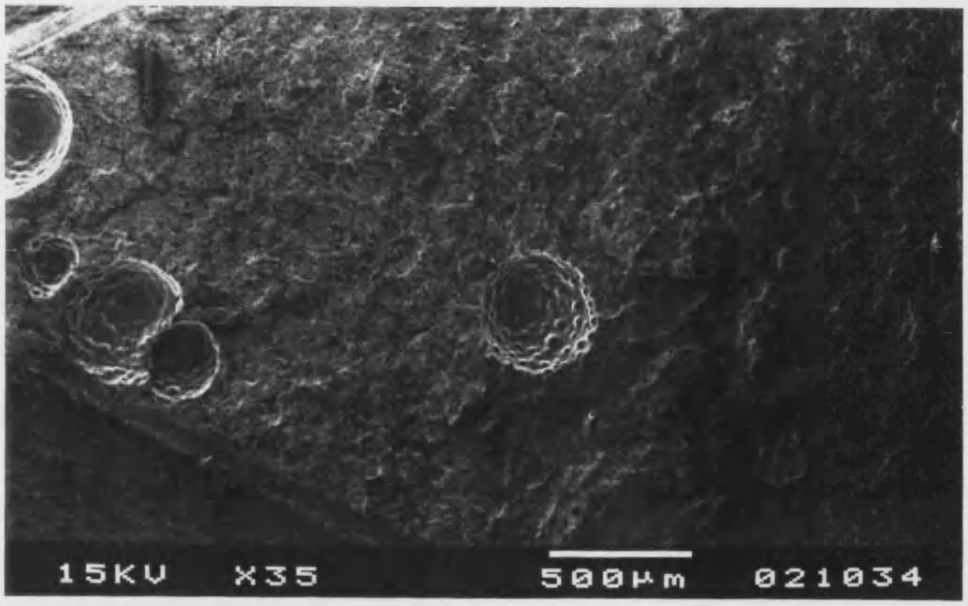


Figure 9.13a : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Lipid at 21°C for 1 Year - Magnification x35.

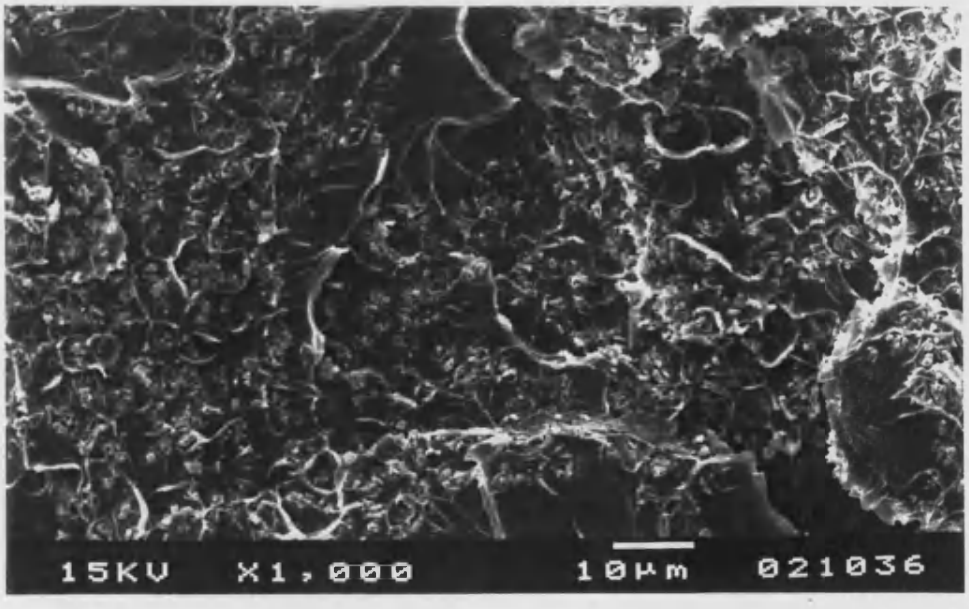


Figure 9.13b : Scanning Electron Micrograph of a WOF Fracture Surface of Normal Radiopaque Cement After Storage in Lipid at 21°C for 1 Year - Magnification x1000.

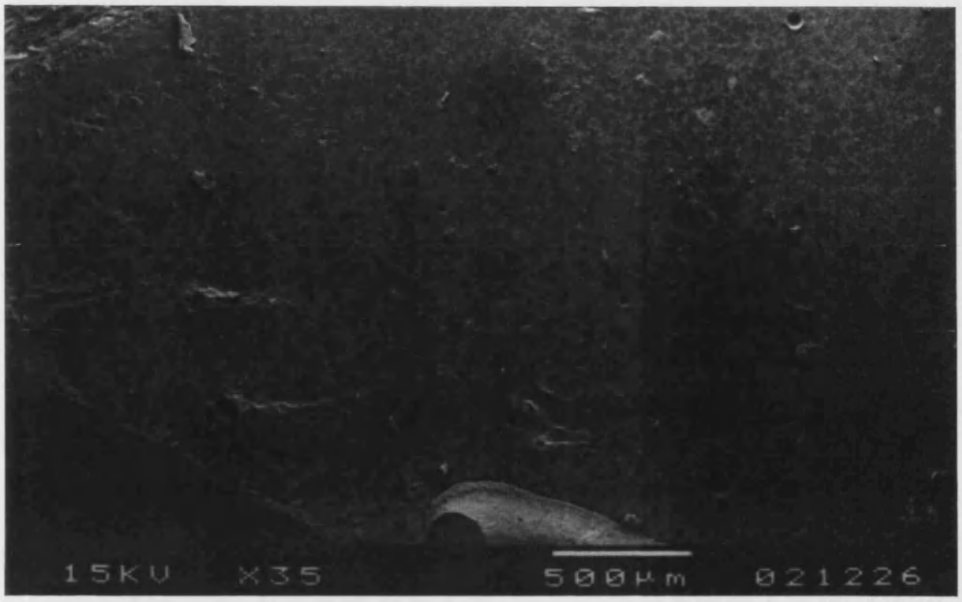


Figure 9.14a : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement Tested Immediately (2 hours) After Heat Treatment - Magnification x35.

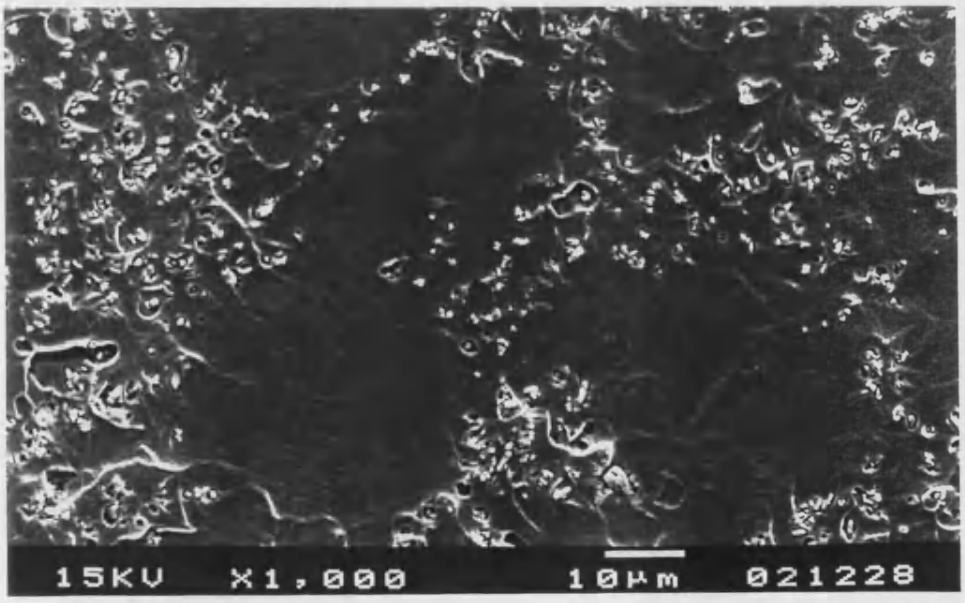


Figure 9.14b : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement Tested Immediately (2 hours) After Heat Treatment - Magnification x1000.

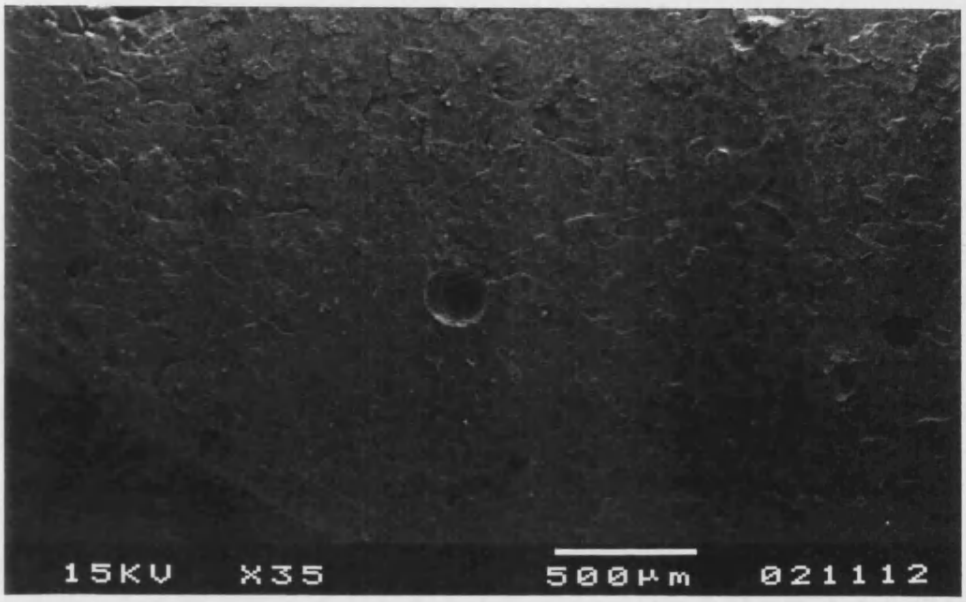


Figure 9.15a : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Air at 21°C for 1 Year - Magnification x35.

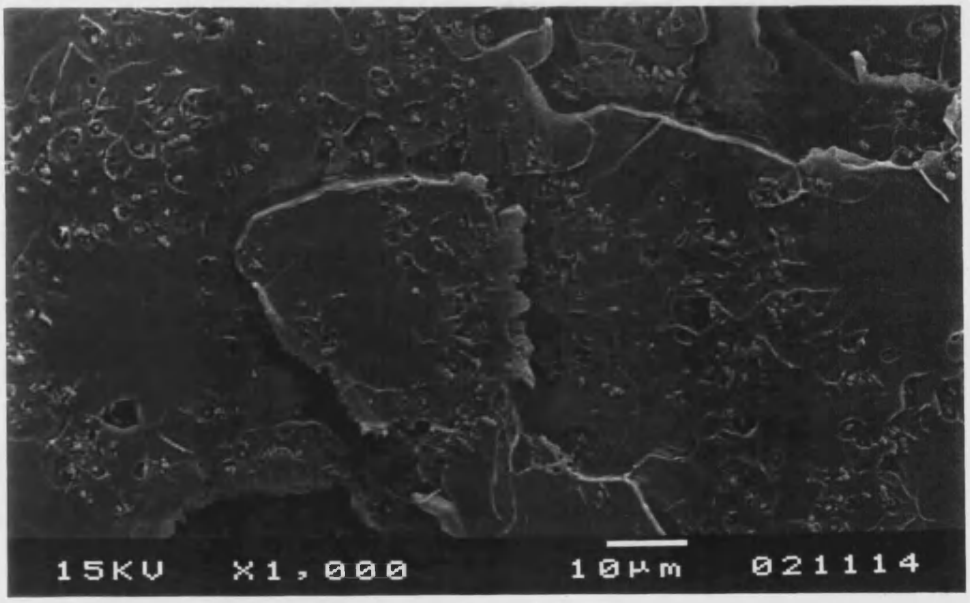


Figure 9.15b : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Air at 21°C for 1 Year - Magnification x1000.

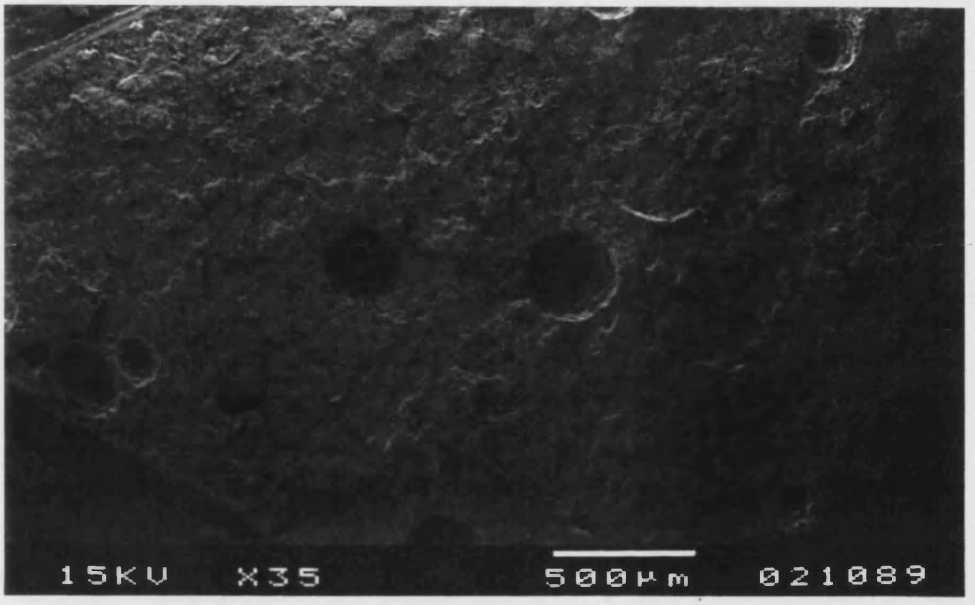


Figure 9.16a : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 21°C for 1 Year - Magnification x35.

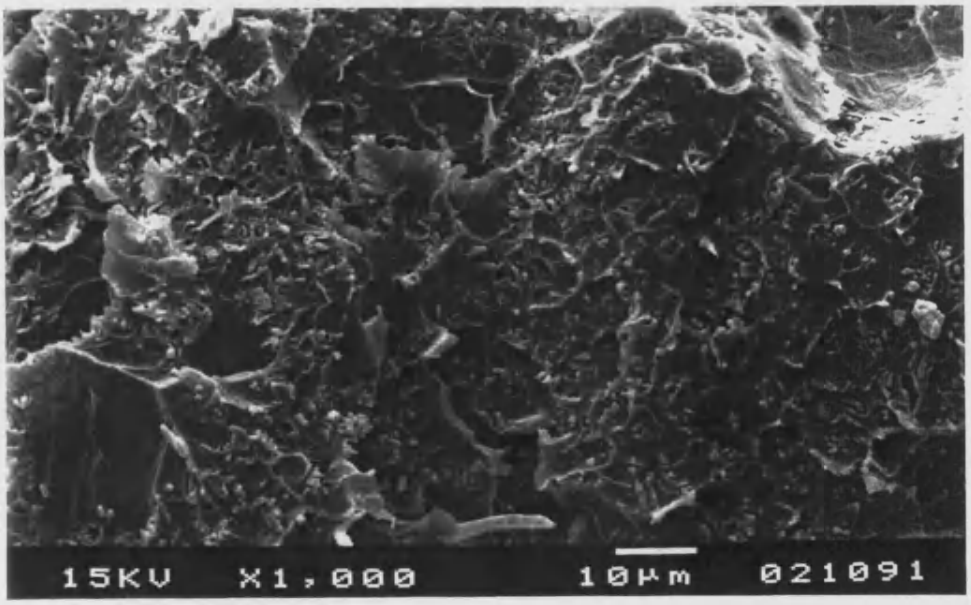


Figure 9.16b : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 21°C for 1 Year - Magnification x1000.

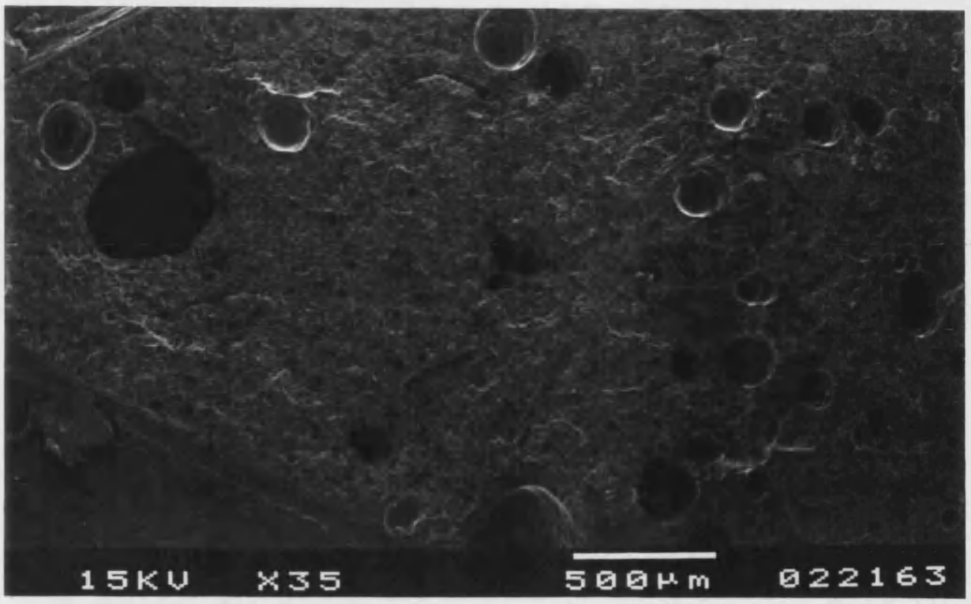


Figure 9.17a : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Ringer's at 21°C for 1 Year - Magnification x35.

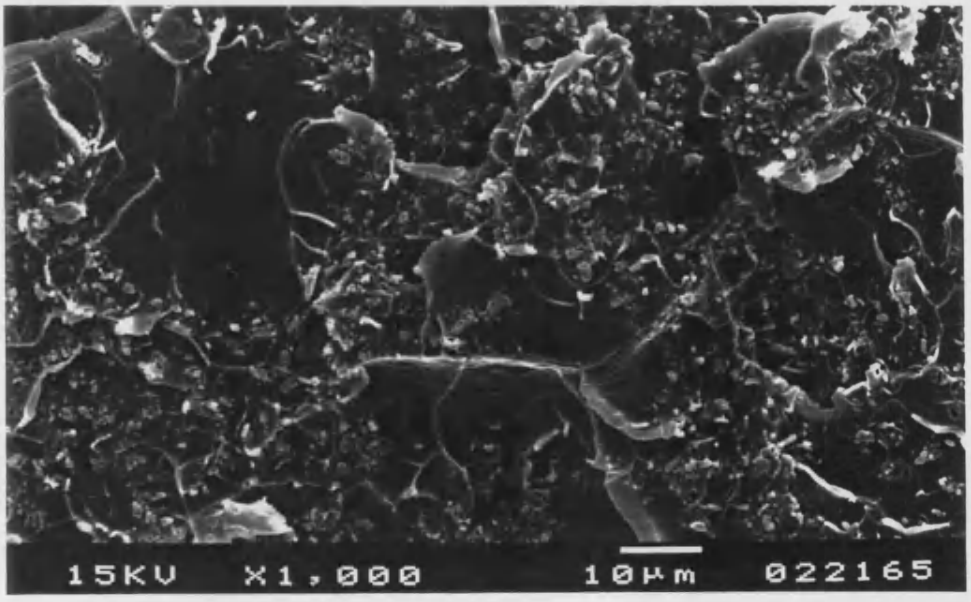


Figure 9.17b : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Ringer's at 21°C for 1 Year - Magnification x1000.

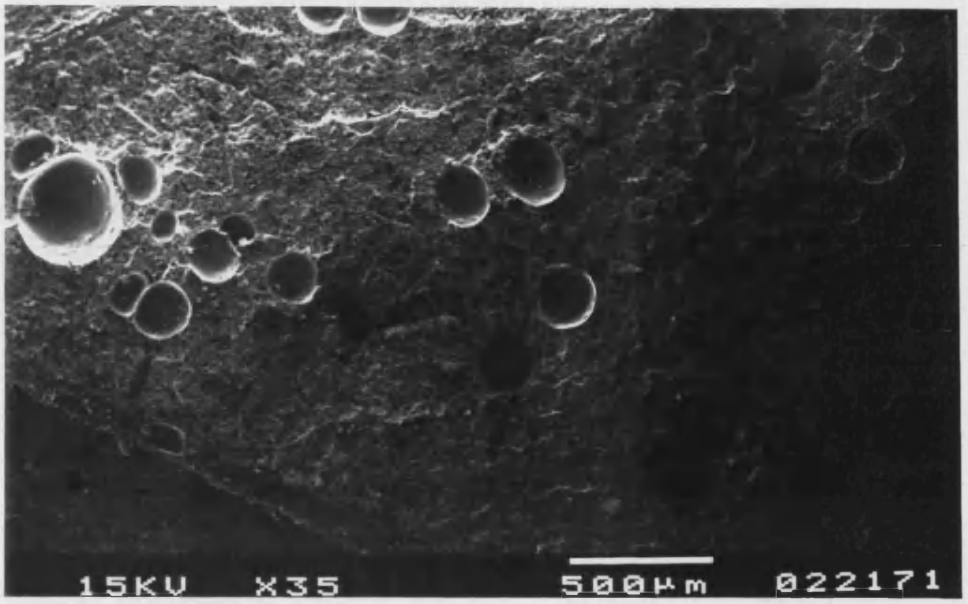


Figure 9.18a : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Lipid at 21°C for 1 Year - Magnification x35.

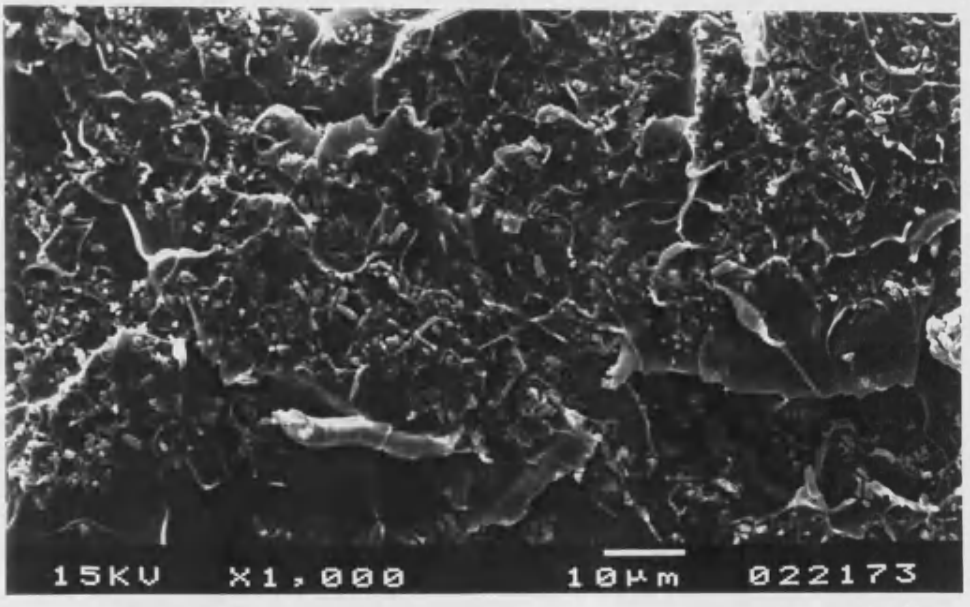


Figure 9.18b : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Lipid at 21°C for 1 Year - Magnification x1000.

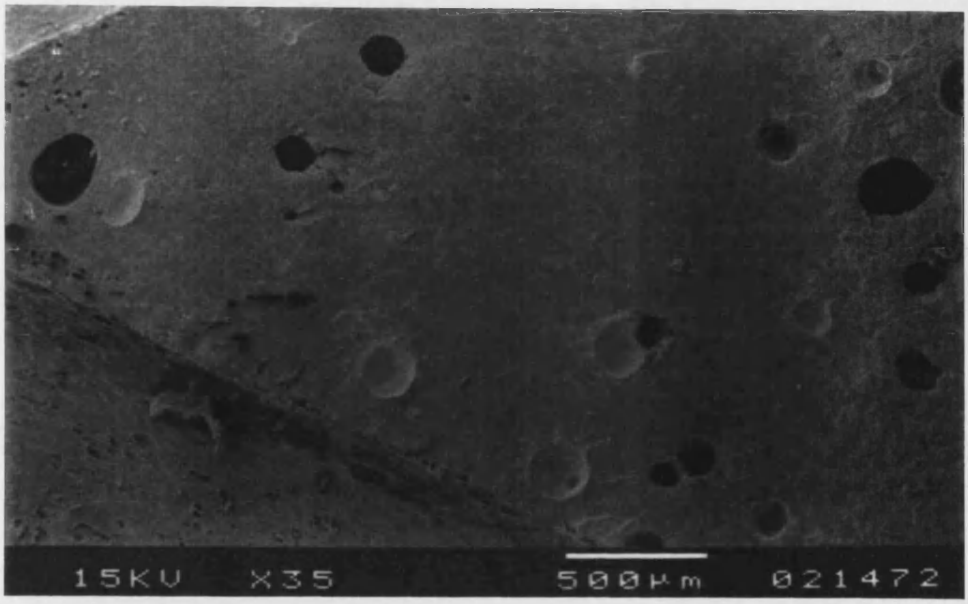


Figure 9.19 : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 21°C for 1 Week - Magnification x35.

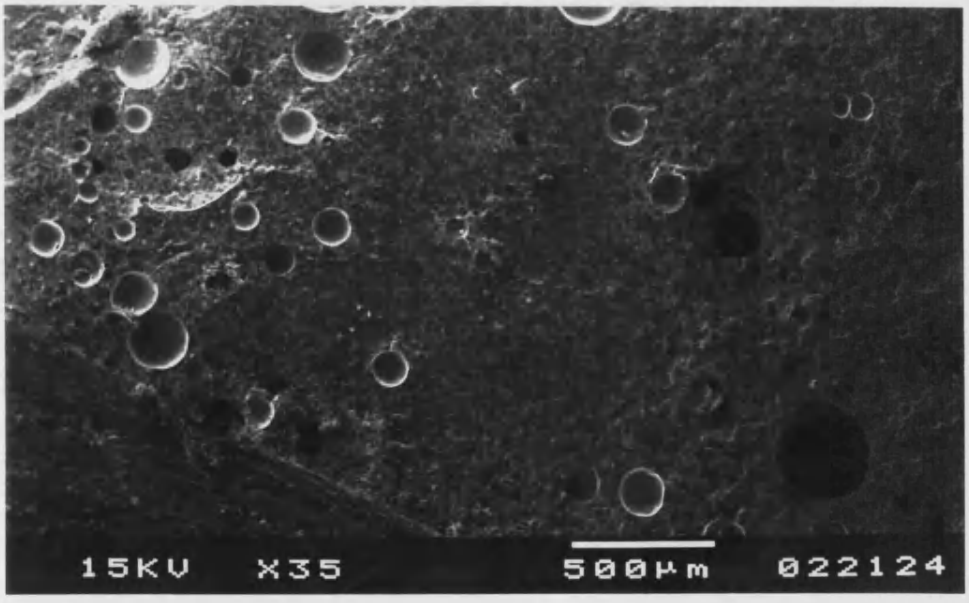


Figure 9.20 : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 37°C for 1 Week - Magnification x35.

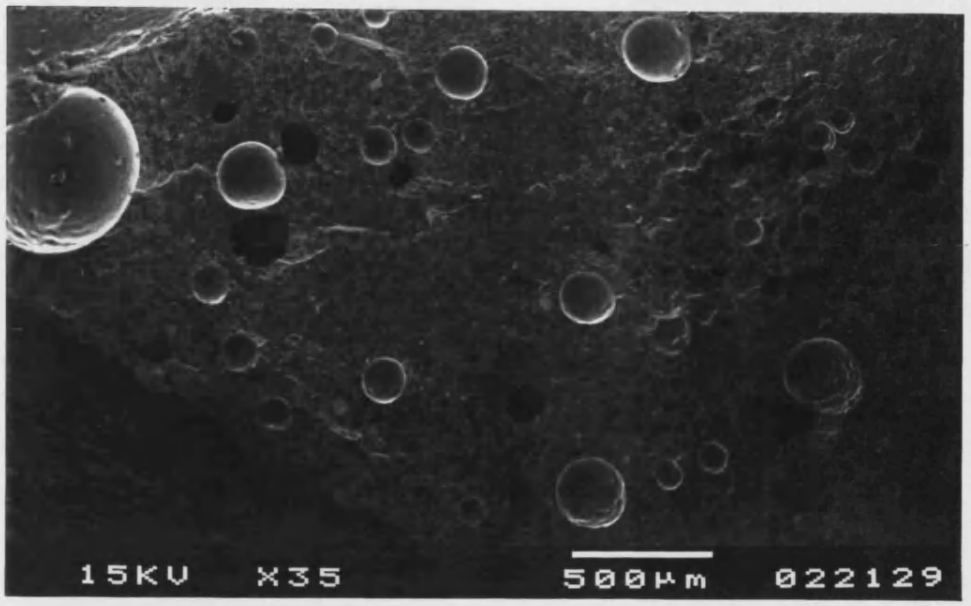


Figure 9.21 : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 21°C for 3 Weeks - Magnification x35.

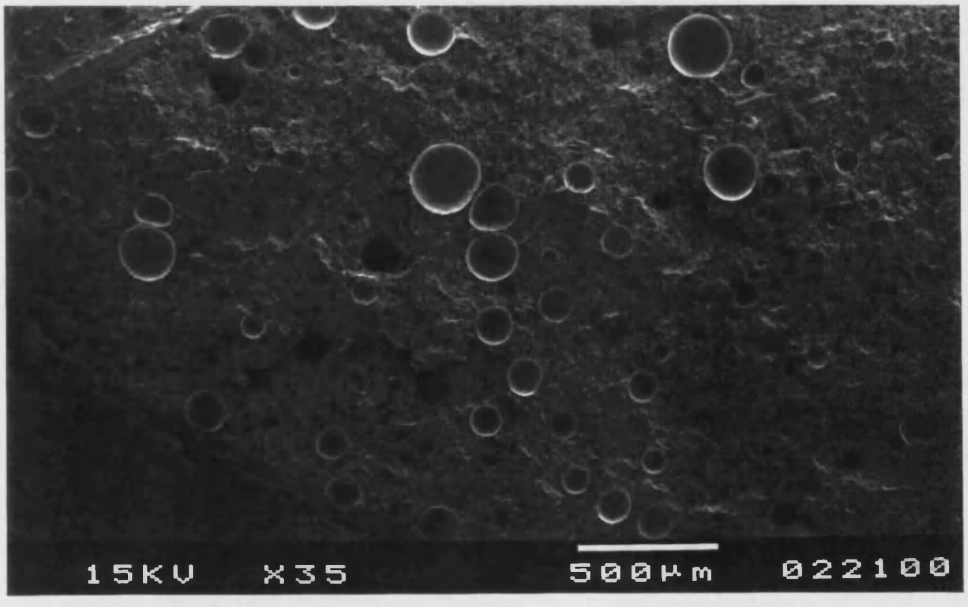


Figure 9.22 : Scanning Electron Micrograph of a WOF Fracture Surface of Fully Cured Radiopaque Cement After Storage in Water at 37°C for 3 Weeks - Magnification x35.

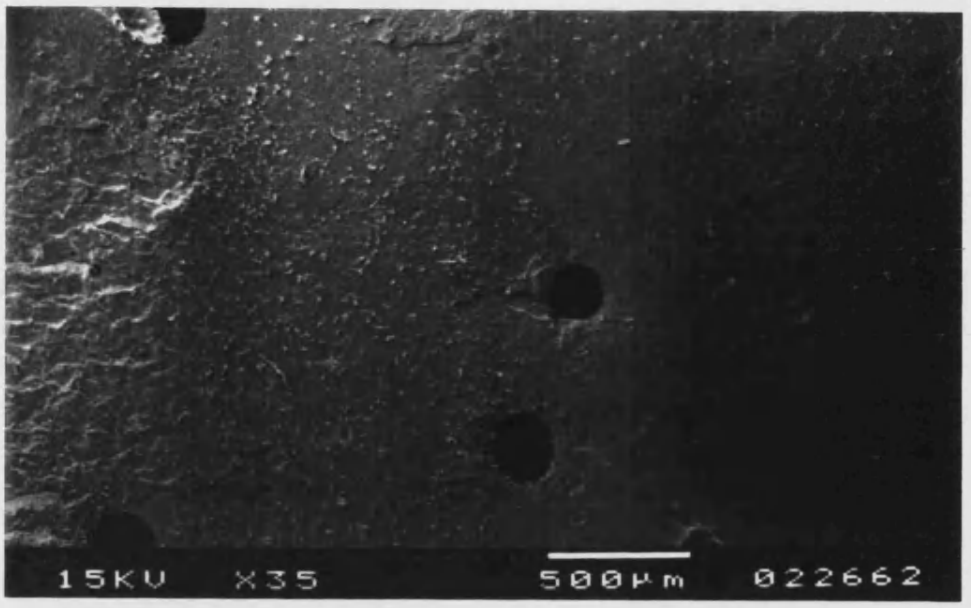


Figure 9.23a : Scanning Electron Micrograph of a Rapid Fracture Surface of Normal Radiopaque Cement After Storage in Air at 21°C for 1 Week - Magnification x35.

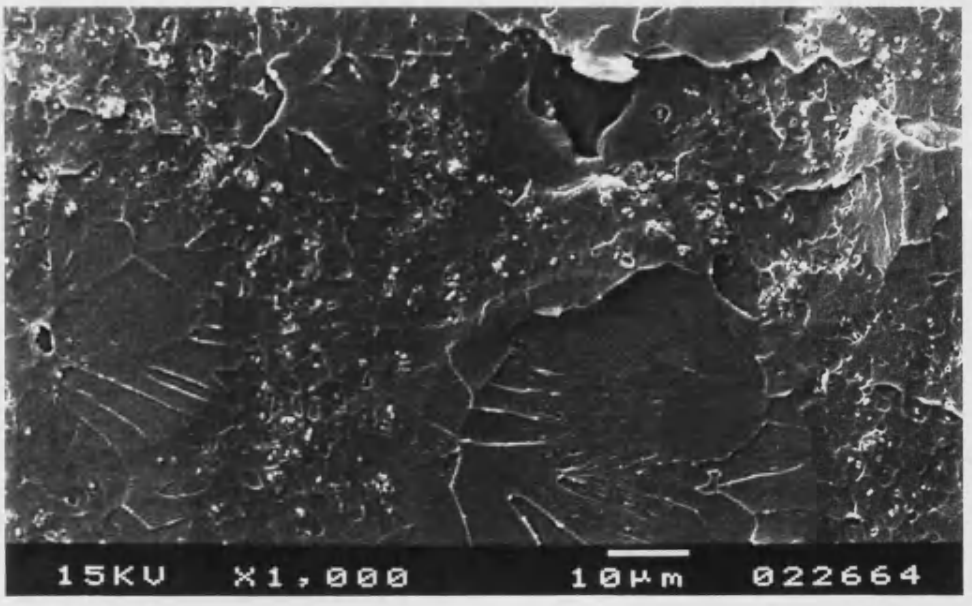


Figure 9.23b : Scanning Electron Micrograph of a Rapid Fracture Surface of Normal Radiopaque Cement After Storage in Air at 21°C for 1 Week - Magnification x1000.

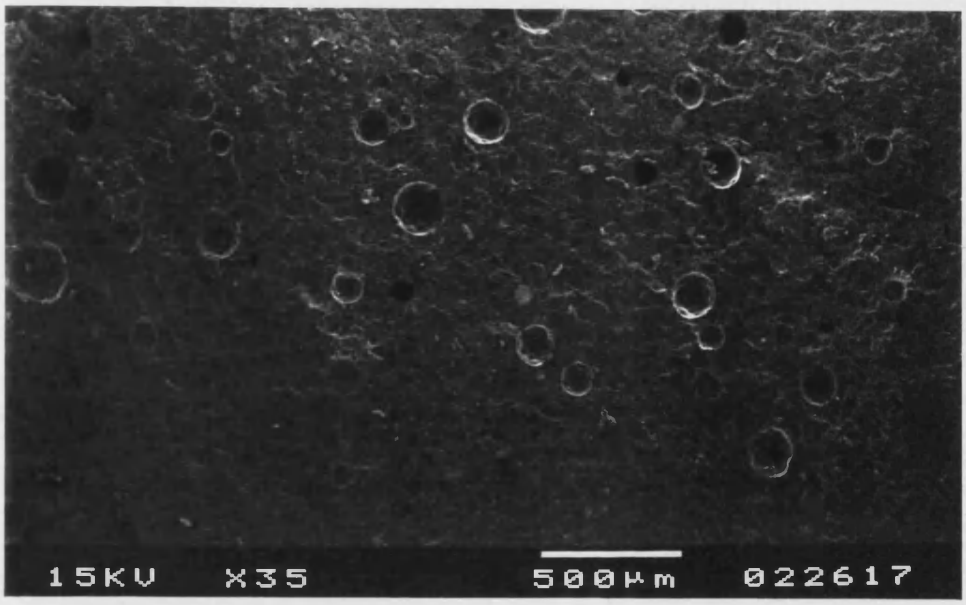


Figure 9.24a : Scanning Electron Micrograph of a Rapid Fracture Surface of Normal Radiopaque Cement After Storage in Water at 21°C for 3 Months - Magnification x35.

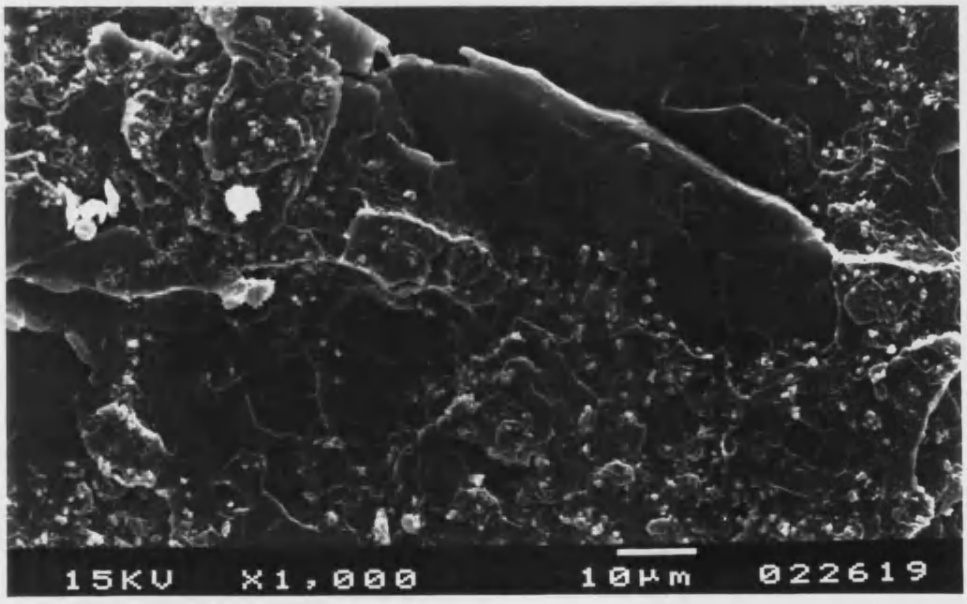
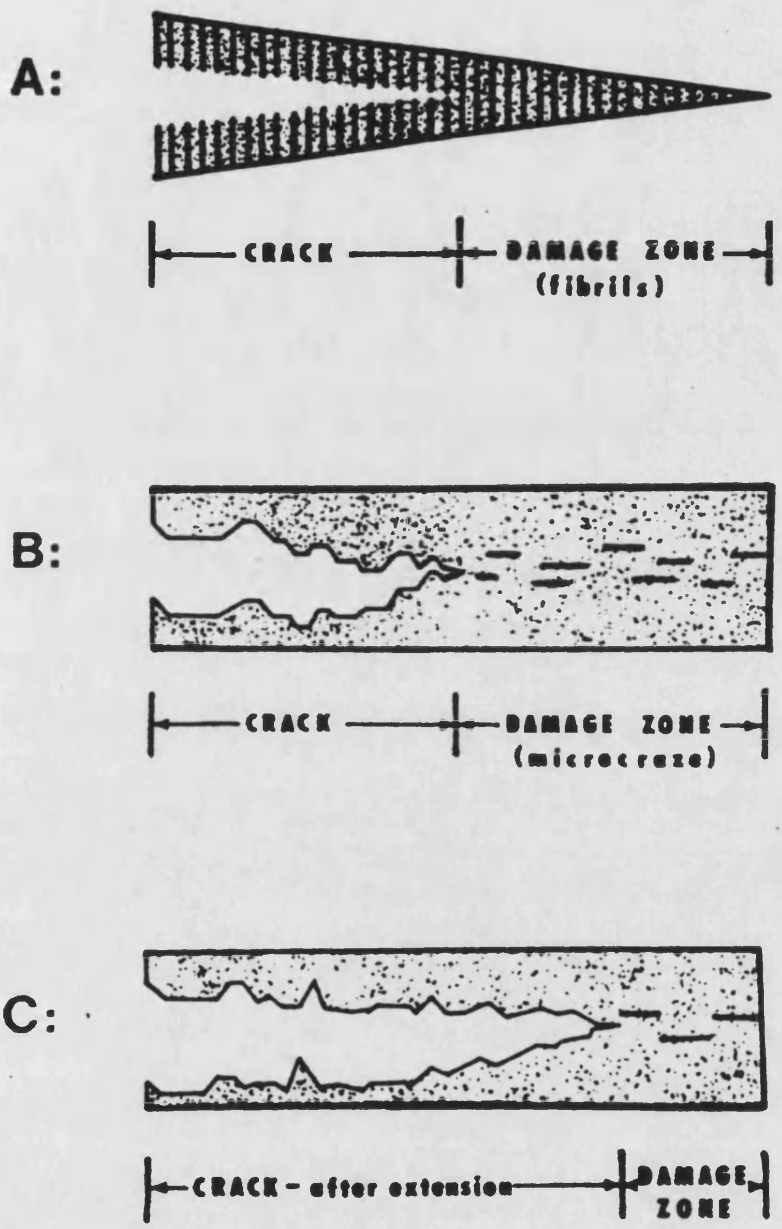


Figure 9.24b : Scanning Electron Micrograph of a Rapid Fracture Surface of Normal Radiopaque Cement After Storage in Water at 21°C for 3 Months - Magnification x1000.



A schematic of possible crack propagation mechanisms in PMMA bone cement. (A) If the polymer is of sufficiently high molecular weight, a damage zone will form where fibrils span the crack surfaces. When the stress across the fibrils is great enough, the fibrils will break, and the crack extends. (B) If the molecular weight of the polymer is not high enough to form fibrils across the damage zone, the crack tip may be preceded by a microcraze shower. (C) As the crack opens, the microcrazes coalesce and the crack extends.

Figure 9.25 : Schematic Diagram Showing the Mechanism of Microcrazing.

(After Topoleski, Ducheyne and Cuckler, 1990)

10. CONCLUSIONS

10.1 Summary of the Thesis

This thesis has shown that the individual storage media and temperatures had significantly different effects on the fracture of behaviour of bone cement. In particular, specimens stored in the fluid media behaved in a more ductile manner than those stored in air, and specimens stored at 37°C behaved in a more brittle manner than those stored at 21°C. Theories for these differing effects are summarised below ;

10.1.1 Normal Cement

The WOF of normal bone cement was found to be increased by the absorption of molecules of low molecular mass liquids, and to be decreased by the leaching of residual monomer from the polymer network. Thus when samples were stored in the fluid media, environmental ingress occurred which led to an increase in the WOF. However, storage of samples in lipid as opposed to water, or at 37° as opposed to 21°C, resulted in the greatest monomer losses which caused a reduction in the WOF. This led to the WOF for samples stored in lipid being less than that for those stored in water, and the WOF for samples stored at 37°C being less than that for samples stored at 21°C, despite the environmental ingress being slightly greater at the elevated temperature. There appeared to be a decrease in the WOF with long-term storage (2 years) which could not be explained in terms of the environmental ingress, the residual monomer content, nor the molecular mass of the cement (see below).

10.1.2 Fully Cured Cement

As with normal cement, the WOF of fully cured cement was increased by the absorption of molecules of the storage fluids. Since the residual monomer had been eliminated as a variable with the heat treated cement, there was little difference between storage of samples in water and storage in lipid. Also, for short storage periods (up to 6 months), samples stored at 37°C had a higher WOF than samples stored at 21°C due to the increased environmental ingress at the higher temperature

without increased leaching of any residual monomer. However, with long-term storage (over 6 months) the samples stored at 37°C experienced a decrease in WOF much earlier than samples stored at 21°C. Again this decrease could not be explained in terms of the environmental ingress, the residual monomer content, nor the molecular mass of the cement. It was postulated that this decrease in WOF was due to a reorganisation of the polymer network, termed physical aging (which increased the modulus of the cement, thus decreasing the resistance to crack growth). This process occurred much more readily at the higher storage temperature, and had a greater influence on the heat treated cement than it did on the normal cement.

10.2 Major Conclusions

It has been shown in this study that:

1) The post-curing chemical changes occurring within bone cement have a significant influence on the fracture behaviour of the material. As with dental acrylics, the mechanical properties of acrylic bone cement are influenced by the leaching of low molecular mass species from within the cement mass, and by the absorption of other low molecular mass species from the environment surrounding the cement.

2) There was a significant decrease in the WOF of acrylic bone cement with long term storage, which would be consistent with an associated increase in the elastic modulus of the material. This decrease in WOF could not be attributed to post-curing chemical changes occurring within the bone cement mass. It is therefore postulated that the decrease in WOF is a result of physical changes occurring with the cement, leading to a gradual reduction in the free volume of the cement and an associated embrittlement of the material.

3) Storage of bone cement at physiological temperatures as opposed to laboratory temperature was shown to have a significant influence on the post-curing chemical

changes within bone cement and hence a significant effect on its fracture behaviour. Samples of normal cement stored in air at laboratory temperature had WOF values 25% higher than samples stored in air at body temperature. For samples stored in the fluid media, those stored at laboratory temperature had WOF values up to 20% higher than samples stored at physiological temperatures.

4) The physiological salts have been shown to have no effect on the post-curing chemical changes which take place within bone cement, and hence have no effect on the fracture behaviour of bone cement.

5) Storage of samples in lipid was found to allow easier leaching of the low molecular mass species from within the cement mass, which resulted in a lower WOF than that obtained when samples were stored in water. Samples of normal cement which were stored in lipid had WOF values which were generally 10% lower than for samples which were stored in the water based media.

6) Many of the previous studies which have characterised the post-curing chemical changes and the mechanical properties of bone cement have been performed under laboratory conditions, in air at ambient temperature. However, this thesis has shown that the *in vivo* environment significantly influences both the chemistry and the mechanical behaviour of bone cement. Hence it is essential that future studies of bone cement attempt to replicate the physiological situation as closely as possible.

11. FUTURE WORK

11. Future Work

The test procedures used in this study were a model of the *in vivo* environment, and in light of the findings of this study several enhancements to bring the model closer to the physiological situation are suggested :

1) In the model used in this study the specimens were stored in the various environments with no mechanical loading on them. In vivo the bone cement would experience dynamic loading during locomotion which could accelerate the uptake of the fluids due to the resultant pumping action of the polymer chains. The cyclic stresses on the cement may also lead to accelerated degradation of the polymer due to the hostile environment. It therefore suggested that WOF tests be performed on cement which has been stored under comparative storage conditions to those used in this study, but where the samples were subjected to simple cyclic loading from zero load up to 3500N (approximately 5 times an average body weight of 70kg) compressive load at a rate of 1 Hz.

2) As discussed in section 4.2.1, it has been shown that the fracture energy of bone cement can be significantly increased if the crack tip is in intimate contact with water. Therefore, measuring the WOF in the storage environments to establish if the fluids plasticised the crack tip may influence the fracture behaviour of the cement, and would also bring the model closer to the physiological situation.

3) Since bone cement is a visco-elastic material its properties are rate and temperature dependant, so testing the WOF at body temperature as opposed to laboratory temperature may again influence the fracture behaviour of the cement, and would be a further enhancement to our model.

4) To obtain an indication of the effect of storage of the cement *in vivo*, would require either evaluation of the WOF of explanted cement, or the evaluation of samples which had been implanted into animals. The problem with explanted cement is that it is difficult to obtain samples which are of the required geometry for WOF tests, and any machining to produce such specimen would remove the cement which had been in

direct contact with the bony tissue. There is also the added difficulty of the entrapment of blood and bone debris, which could again influence the results. Testing of samples which had been produced in the laboratory, then implanted into animals, although not representing the human situation, would give a very good indication of the effect of storage under physiological conditions. If, however, the effect of curing the cement *in vivo* was to be investigated then problems as discussed above for explanted cement would be encountered.

Further testing which this study has highlighted as interesting for future work includes:

1) It would be informative to perform additional longer term WOF tests on the normal cement to ascertain whether the observed decrease in the fracture resistance with storage for 2 years continues for longer storage periods.

2) The determination of the free volume of cement samples after different lengths of storage to see if there is a reorganisation of the polymer chains with time due to physical aging, which could account for the observed decreases in WOF with long term storage of cement.

This study has shown that the residual monomer in bone cement has a plasticising effect on the material, thus increasing its resistance to crack growth. It has also been suggested in the literature (see section 7.2.1) that the monomer may have a toxic effect on the surrounding bone tissue as it leaches from the cement. If this monomer could be trapped within the cement structure, so that it was still able to move between the polymer chains and hence retain its plasticising effect, but could not leach into the bone tissue, then both the toxicity and the fracture behaviour of the cement would be significantly improved. A future development of bone cements may therefore be to modify the methylmethacrylate monomer, or to look at different monomers which are not soluble in either water or fat.

12. REFERENCES

12. References

Albrektsson T., (1985). In vivo effects of bone cement on circulation, fat cells and bone. *Acta. Orthop. Scand.*, Vol. 56, pp. 172-173.

Andersson G.B.J., Freeman M.A.R., Swanson S.A.V., (1972). Loosening of the cemented acetabular cup in total hip replacement. *Journal of Bone and Joint Surgery*, Vol. 54-B, pp. 590-599.

ASTM, F451-76, (1976). Standard specification for acrylic bone cements. American Society for Testing and Materials, Philadelphia, Penn.

Bargar W.L., Brown S.A., Paul H.A., Voegli T., Hseih Y., Sharkey N., (1986). In vivo versus in vitro polymerisation of acrylic bone cement: effect on material properties. *Journal of Orthopaedic Research*, Vol. 4, pp. 86-89.

Barker L.M., (1977). A simplified method for measuring plane strain fracture toughness. *Engineering Fracture Mechanics*, Vol. 9, pp. 361-369.

Basker R.M., Collier J., Smith I., Bartle K.D., Frere B., Wong L., (1989). Variation of residual monomer content of poly(methylmethacrylate) dental resins with time, and the influence of water immersion. *Clinical Materials*, Vol. 4, pp. 173-182.

Bayne S.C., (1974). Master's Thesis, Northwestern University, Department of Biological Materials.

Bayne S.C., Lautenschlager E.P., Compere C.L., Wildes R., (1975). Degree of polymerisation of acrylic bone cement. *Journal of Biomedical Materials Research*, Vol. 9, pp. 27-34.

Bayne S.C., Lautenschlager E.P., Greener E.H., Meyer P.R., (1977). Clinical influences on bone cement monomer release. *Journal of Biomedical Materials Research*, Vol. 11, pp. 859-869.

Beaumont P.W.R., (1976).Fracture of acrylic bone cement. *The Lancet*, Oct. 16, pp. 860-861.

Beaumont P.W.R., (1977). The strength of acrylic bone cements and acrylic cement-stainless steel interfaces. Part 1. The strength of acrylic bone cement containing second phase dispersions. *Journal of Materials Science*, Vol. 12, pp. 1845-1852.

Beaumont P.W.R., (1979). Fracture processes in acrylic bone cement containing barium sulphate dispersions. *Journal of Biomedical Engineering*, Vol. 1, pp. 147-152.

Beaumont P.W.R., Young R.J., (1975). Slow crack growth in acrylic bone cement. *Journal of Biomedical Materials Research*, Vol. 9, pp. 423-439.

Beaumont P.W.R., Young R.J., (1977). Strength and fracture of acrylic bone cement and cement-metal interfaces. *Plastics and Rubber : Materials and Applications*, Vol. Feb., pp. 2-6.

Beech D.R., (1975). Molecular weight distribution of denture base acrylic. *Journal of Dentistry*, Vol. 3, p. 19.

Benbow J.J., (1961). Stable crack propagation in plastics. *Proceedings of the Physics Society*, Vol. 78, pp. 970-978.

Bevan E.M., Earnshaw R., (1968). The role of water sorption in the solvent crazing of acrylic resins. *Australian Dental Journal*, Vol. 13, pp. 265-273.

Beverly G.M., (1990). ICI Chemicals and Polymers Ltd., Private communication.

Black J., (1988). "Orthopaedic Biomaterials in Research and Practice". Churchill Livingstone, New York.

Bloch B., Haken J.K., Hastings G.W., (1971). Cold-curing cements in orthopaedic surgery. *The Medical Journal of Australia*, Vol. 9, pp.93-94.

Bonfield W., (1987). Materials for the replacement of osteoarthritic hip joints. *Metals and Materials*, Vol. 3, pp. 712-716.

Bonfield W., (1993). Polymers for medical applications. Paper presented at Polymer Science and Technology Conference, 21-23 April, University of Leeds, Leeds, UK. Unpublished.

Brand R.A., Pederson D.R., Yoder S.A., (1986). How definition of "loosening" affects the incidence of loose total hip reconstructions. *Clinical Orthopaedics and Related Research*, Vol. 210, pp. 185-191.

Brauer G.M., Steinberger D.R., Stansbury J.W., (1986). Dependence of curing time, peak temperature, and mechanical properties on the composition of bone cement. *Journal of Biomedical Materials Research*, Vol. 20, pp. 839-852.

Brauer G.M., Termini D.J., Dickson G., (1977). Analysis of the ingredients and determination of the residual components of acrylic bone cements. *Journal of Biomedical Materials Research*, Vol. 11, pp. 577-607.

Brown S.A., Sharkey N.A., Bargar W.L., Paul H.A., Voegli T.L., Hseih Y.L., (1984). Properties of in vitro and in vivo cured acrylic bone cement. In "Biomaterials and Biomechanics 1983", Ducheyne P. *et al* (eds.), Elsevier, Amsterdam, pp. 13-18.

Brydson J.A., (1975). Acrylic Plastics. In "Plastic Materials", Newnes-Butterworths, London, pp. 328-346.

Cameron H.U., Mills R.H., Jackson R.W., Macnab I., (1974). The structure of polymethylmethacrylate cement. *Clinical Orthopaedics and Related Research*, Vol. 100, pp. 287-291.

Caul H.J., Sweeney W.T., Paffenbarger G.C., (1956). Relationship between residual monomer and some properties of self-curing dental resins. *Journal of American Dental Association*, Vol. 53, pp. 60-63.

Causton B.E., (1975). Fracture mechanics of dental poly(methylmethacrylate). *Journal of Dental Research*, Vol. 54, pp. 339-343.

Charnley J., (1970). Acrylic Cement in Orthopaedic Surgery, E and S Livingstone, Edinburgh.

Charnley J., (1975). The histology of loosening between acrylic cement and bone. *Journal of Bone and Joint Surgery*, Vol. 57-B, p. 245.

Chiba J., Maloney W., Horikoshi M., McIntyre L., Rubash H., (1993). Biochemical and morphological analyses of activated human macrophages and fibroblasts by human polyethylene particles. *Transactions of 39th Annual Meeting of the Orthopaedic Research Society*, February 15-18, San Francisco, California, USA, p. 270.

Christian G.D., O'Reilly J.E., (eds.), (1986). Instrumental Analysis, 2nd edition, Allyn and Bacon Inc., Boston, pp. 658-725.

Clarke I.C., Campbell P., (1988). Interface failure dynamics : osteoclastic and macrophagic bone loss. In "Progress in Bioengineering", Paul J.P., Barbenel J.C., Courtney J.M., Kenedi R.M. (eds.), Adam Hilger, Bristol, pp. 104-115.

Cooke F.W., Tsai Y.H., Marrero T.R., Yasuda H.K., (1991). Improved bone cement strength by chemically coupling radiopacifier additions to the PMMA. *Transactions of the 17th Annual Meeting of the Society for Biomaterials*, May 1-5, Scottsdale, Arizona, USA, p. 46.

Coventry M.B., Beckenbaugh R.D., Nolan D.R., Ilstrup D.M., (1974). 2,012 total hip arthroplasties : a study of postoperative course and early complications. *Journal of Bone and Joint Surgery*, Vol. 56-A, pp. 273-284.

Davidge R.W., Phillips D.C., (1972). The significance of impact data for non-metallic materials. *Journal of Materials Science*, Vol. 7, pp. 1308-1314.

Davidson J.A., Lynch G.E., Locke L., (1988). Slow-rising load environmental stress cracking susceptibility testing of polymethylmethacrylate and UHMWPE in various environments. *Proceedings of the 7th Southern Biomedical Engineering Conference*, October 27-28, Greenville, South Carolina, USA.

Davies S., (1989). North Hill Plastics Ltd., Private communication.

DeWijn J.R., Sloof T.J.J.H., Driessens F.C.M., (1975). Characterization of bone cements. *Acta Orthop Scand.*, Vol. 46, pp. 38-51.

Ferracane J.L., (1981). The effects of fat incorporation on conventional and gun injected bone cments. *Paper submitted for presentation at Society for Biomaterials*, May, Troy, New York, USA.

Fifield R., (1987). New lives for painful hips. *New Scientist*, Vol. 10, pp. 35-38.

Fisher J., (1993). Private communication.

Freeman M.A.R., Bradley G.W., Revell P.A., (1982). Observations upon the interface between bone and polymethylmethacrylate cement. *Journal of Bone and Joint Surgery*, Vol. 64-B, p. 489.

Freitag T.A., Cannon S.L., (1976). Fracture Characteristics of acrylic bone cements. I. Fracture Toughness. *Journal of Biomedical Materials Research*, Vol. 10, pp. 805-828.

Gharpuray V.M., Keer L.M., Lewis J.L., (1990). Cracks emanating from circular voids or elastic inclusions in PMMA near a bone-implant interface. *Journal of Biomechanical Engineering*, Vol. 112, pp. 22-28.

Gilding D.K., Emery I.H., (1977). The molecular characterisation of acrylic bone cement in clinical use. *Journal of Bone and Joint Surgery*, Vol. 59-B, p. 502.

Gentil B., Paugam C., Wolf C., Lienhart A., Augereau B., (1993). Methylmethacrylate plasma levels during total hip arthroplasty. *Clinical Orthopaedics and Related Research*, Vol. 287, pp. 112-116.

Gutteridge D.L., (1993). The effect of variations in fibre length on the impact strength of poly(methyl methacrylate) resin reinforced with ultra-high-modulus polyethylene fibre. *Clinical Materials*, Vol. 12, pp. 137-140.

Haas S.S., Brauer G.M., Dickson G., (1975). A characterisation of polymethylmethacrylate bone cement. *Journal of Bone and Joint Surgery*, Vol. 57-A, pp. 380-391.

Hansen D., Jensen J.S., (1990). Prechilling and vacuum mixing not suitable for all bone cements. *Journal of Arthroplasty*, Vol. 5, pp. 287-290.

Harris B., (1989). Private communication.

Harris W.H., McCarthy J.C. Jr., O'Neill D.A., (1982). Femoral component loosening using contemporary techniques of femoral cement fixation. *Journal of Bone and Joint Surgery*, Vol. 64-A, pp. 1063-1067.

Healy W.L., Wasilewski S.A., Pfeifer B.A., Kurtz S.R., Hallack G.N., Valerio M., Valeri R., (1993). Methylmethacrylate monomer and fat content in shed blood after total joint arthroplasty. *Clinical Orthopaedics and Related Research*, Vol. 286, pp. 15-17.

Heftmann E, (1967). Chromatography, 2nd edition, Reinhold Publishing Corporation, New York, pp. 182-209.

Hill R.G., Bates J.F., Lewis T.T., Rees N., (1984). The fracture of acrylic polymers in water. *Journal of Materials Science*, Vol. 19, pp. 1904-1916.

Holm N.J., (1977). The modulus of elasticity and flexural strength of some acrylic bone cements. *Acta Orthop. Scand.*, Vol. 48, pp. 436-442.

Horowitz S.M., Doty S.B., Rapuano B., Burstein A.H., (1993). Role of the macrophage and the osteoblast in mediator production at the interface in aspetic loosening. *Transactions of 39th Annual Meeting of the Orthopaedic Research Society*, February 15-18, San Francisco, California, USA, p. 268.

Howmedica, (1989). Manufacturers literature, North Hill Plastics, 49 Grayling Road, London.

Huggett R., Bates J.F., Packham D.E., (1983). The molecular weight determination of poly(methylmethacrylate) denture base materials. *Laboratory Practice*, Vol. 32, pp. 74-78.

Huggett R., Bates J.F., Packham D.E., (1987). The effect of curing cycle upon the molecular weight and properties of denture base materials. *Dental Materials*, Vol. 3, pp. 107-112.

ISO 4049 : 1988 (E), (1988). Dentistry - Resin-based filling materials, International Standards Organisation, p. 8.

Jaffe W.L., Rose R.M., Radin E.L., (1974). On the stability of the mechanical properties of self-curing acrylic bone cement. *Journal of Bone and Joint Surgery*, Vol. 56-A, pp. 1711-1714.

Jagger R.G., (1978). Effect of the curing cycle on some properties of a polymethylmethacrylate denture base material. *Journal of Oral Rehabilitation*, Vol. 5, pp. 151-157.

James S.P., Jasty M., Davies J., Piehler H., Harris W.H., (1992). A fractographic investigation of PMMA bone cement focusing on the relationship between porosity reduction and increased fatigue life. *Journal of Biomedical Materials Research*, Vol. 26, pp. 651-662.

Jast M., Maloney W.J., Bragdon C.R., O'Connor D.O., Haire T., Harris W., (1991). The initiation of failure in cemented femoral components of hip arthroplasties. *Journal of Bone and Joint Surgery*, Vol. 73-B, pp. 551-558.

Jasty M., Smith E., (1992). Wear particles of total joint replacements and their role in periprosthetic osteolysis. *Current Opinion in Rheumatology*, Vol. 4, pp. 204-209.

Jefferiss C.D., Lee A.J.C., Ling R.S.M., (1975). Thermal aspects of self-curing polymethylmethacrylate. *Journal of Bone and Joint Surgery*, Vol. 57-B, pp. 511-518.

Johanson N.A., Bullough P.G., Wilson P.D., Salvati E.A., Ranawat C.S., (1987). The microscopic anatomy of the bone-cement interface in failed total hip arthroplasties. *Clinical Orthopaedics and Related Research*, Vol. 218, pp. 123-135.

Johnson J.A., Jones D.W., (1991). Influence of composition of methylmethacrylate copolymers on mechanical properties. *Transactions of the 17th Annual Meeting of the Society for Biomaterials*, May1-5, Scottsdale, Arizona, USA, p. 49.

Johnson J.A., Provan J.W., Krygier J.J., Chan K.H., Miller J., (1989). Fatigue of acrylic bone cement - effect of frequency and environment. *Journal of Biomedical Materials Research*, Vol. 23, pp. 819-831.

Katz D., (1990). Towards a lasting replacement. Telegraph Young Science Writer Awards 1990, The Daily Telegraph.

Krause W., Mathis R.S., (1988). Fatigue properties of acrylic bone cements : Review of the literature. *Journal of Biomedical Materials Research : Applied Biomaterials*, Vol. 22, No. A1, pp. 37-53.

Kusy R.P., (1978). Characterization of self-curing acrylic bone cements. *Journal of Biomedical Materials Research*, Vol. 12, pp. 271-305.

Kusy R.P., Mahan J.R., Turner D.T., (1976). Influence of application technique on microstructure and strength of acrylic restorations. *Journal of Biomedical Materials Research*, Vol. 10, pp. 77-89.

Kusy R.P., Turner D.T., (1974). Characterization of the microstructure of a cold-cured acrylic resin. *Journal of Dental Research*, Vol. 53, p. 948.

Lamb D.J., Ellis B., van Noort R., (1985). The fracture topography of acrylic dentures broken in service. *Biomaterials*, Vol. 6, pp. 110-112.

Lautenschlager E.P., Stupp S.I., Keller J.C., (1984). Structure and properties of acrylic bone cement. In "Functional Behaviour of Orthopaedic Biomaterials. Volume II Applications", Ducheyne P., Hastings G.W. (eds), CRC Press Inc., Boca Raton, pp. 87-119.

Lee A.J.C., Ling R.S.M., (1975). Further studies of monomer loss by evaporation during the preparation of acrylic cement for use in orthopaedic surgery. *Clinical Orthopaedics and Related Research*, Vol. 106, pp. 122-125.

Lee A.J.C., Ling R.S.M., Pearson G.P., (1981). Fixation. In "An Introduction to the Biomechanics of Joints and Joint Replacement", Dowson D., Wright V. (eds.), Mechanical Engineering Publications Ltd., London, pp. 172-187.

Lee A.J.C., Ling R.S.M., Vangala S.S., (1977). The mechanical properties of bone cements. *Journal of Medical Engineering and Technology*, Vol. 2, pp. 137-140.

Lee A.J.C., Ling R.S.M., Wrighton J.D., (1973). Some properties of polymethylmethacrylate with reference to its use in orthopedic surgery. *Clinical Orthopaedics and Related Research*, Vol. 95, pp. 281-287.

Lewis G., (1992). Effect of lithotriptor treatment on the fracture toughness of acrylic bone cement. *Biomaterials*, Vol. 13, pp. 225-229.

Linder L.G., Harthon L., Kullberg L., (1976). Monomer leakage from polymerizing acrylic bone cement. *Clinical Orthopaedics and Related Research*, Vol. 119, pp. 242-249.

Ling R.S.M., (1986). Observations on the fixation of implants to the bony skeleton. *Clinical Orthopaedics and Related Research*, vol. 210, pp. 80-96.

Looney M.A., Park J.B., (1986). Molecular and mechanical property changes during aging of bone cement in vitro and in vivo. *Journal of Biomedical Materials Research*, Vol. 20, pp. 555-563.

Malcolm A.J., (1988). Pathology of long-standing cemented total hip replacements in Charnley's cases. *Journal of Bone and Joint Surgery*, Vol. 70-B, p. 153.

Martens M., Aernoudt E., DeMeester P., Ducheyne P., Mulier J.C., DeLangh R., Kestelijn P., (1974). Factors in the mechanical failure of the femoral component in total hip prosthesis. *Acta. Orthop. Scand.*, Vol. 45, pp. 693-710.

Martin R.J., Johnson J.F., Cooper A.R., (1973). Mechanical properties of polymers : the influence of molecular weight and molecular weight distribution. *Reviews in Macromolecular Chemistry*, Vol. 9, p. 57.

Mayer R.D., Moyle D.D., Sauer B.W., (1983). Fracture of porous polyethylene-bone composite. *Journal of Biomedical Materials Research*, Vol. 17, pp. 59-70.

Meyer P.R., Lautenschlager E.P., Moore B.K., (1973). On the setting properties of acrylic bone cement. *Journal of Bone and Joint Surgery*, Vol. 55-A, pp. 149-156.

Miles A.J., (1989). School of Materials Science Colloquium Presentation. University of Bath, Bath, UK. Unpublished.

Miller J., Burke D.L., Stachiewicz J.W., Kelchay L., (1977). Loosening of joint implant components as a result of failure of polymethylmethacrylate. *Journal of Bone and Joint Surgery*, Vol. 59-B, p. 121.

Moreland J.R., (1988). Mechanisms of failure in total knee arthroplasty. *Clinical Orthopaedics and Related Research*, Vol. 226, pp. 49-64.

Moyle D.D., Bowden R.W., (1984). Fracture of human femoral bone. *Journal of Biomechanics*, Vol.17, pp. 203-213.

Moyle D.D., Welborn J.W., Cooke F.W., (1978). Work to fracture of canine femoral bone. *Journal of Biomechanics*, Vol. 11, pp. 435-440.

Neihart T.R., Li S.H., Flinton R.J., (1988). Measuring fracture toughness of high-impact poly(methylmethacrylate) with the short rod method. *Journal of Prosthetic Dentistry*, Vol. 60, pp.249-253.

Newman J.C., (1984). A review of chevron-notched fracture specimens. In "Chevron-Notched Specimens : Testing and Stress Analysis", Underwood J.H., Freiman S.W., Baratta F.I. (eds.), ASTM Special Technical Publication 855, Philadelphia, pp. 5-31.

Noble P.C., (1983). Selection of acrylic bone cements for use in joint replacement. *Biomaterials*, Vol. 4, pp. 94-100.

Owen A.B., Beaumont P.W.R., (1979). Fracture behaviour of commercial surgical acrylic bone cements. *Journal of Biomedical Engineering*, Vol. 1, pp. 277-280.

Owen A.B., Beaumont P.W.R., (1980). Fracture characteristics of surgical acrylic bone cements. In "Mechanical Properties of Biomaterials", Hastings G.W., Williams D.F. (eds.), John Wiley and Sons Ltd., Chichester, pp. 277-287.

Park J.B., (1983). Acrylic bone cement: *in vitro* and *in vivo* property-structure relationship - a selective review. *Annals of Biomedical Engineering*, Vol. 11, pp. 297-312.

Paterson M., Fulford P, Denham R., (1986). Loosening of the femoral component after total hip replacement. *Journal of Bone and Joint Surgery*, Vol. 68-B, pp. 392-397.

Pearson G.P., Jones D.F., (1978). Chemistry, properties and orthopaedic applications of acrylic cements. *The British Polymer Journal*, Vol. 10, pp. 256-259.

Perek J., Pilliar R.M., (1992). Fracture toughness of composite acrylic bone cements. *Journal of Materials Science : Materials in Medicine*, Vol. 3, pp. 333-344.

Perkins R.D., Lee A.J.C., Ling R.S.M., (1990). Preliminary report on the effect of creep of polymethylmethacrylate (PMMA) bone cement and its relevance to total hip arthroplasty. *Journal of Bone and Joint Surgery*, Vol. 72-B, p. 162.

Petty W., (1980). Methylmethacrylate concentrations in tissues adjacent to bone cement. *Journal of Biomedical Materials Research*, Vol. 14, pp. 427-434.

Pizzoferrato A., Ciapetti G., Stea S., Toni A., (1991). Cellular events in the mechanisms of prosthesis loosening. *Clinical Materials*, Vol. 7, pp. 51-81.

Price G., (1992). Private communication.

Public Eye, (1993). The high price of hips. BBC News and Current Affairs Television Program.

Rimnac C.M., Wright T.M., McGill D.L., (1986). The effect of centrifugation on the fracture properties of of acrylic bone cements. *Journal of Bone and Joint Surgery*, Vol. 68-A, pp. 281-287.

Rogers L.L., Moyle D.D., (1988). Effect of specimen size on work of fracture measurements. *Journal of Biomechanics*, Vol. 21, pp. 919-926.

Rose R.M., Litsky A.S., (1989). Biomechanical considerations in the loosening of hip replacement prostheses. In "Current Perspectives on Implantable Devices - Volume I", Williams D.F. (ed.), Jai Press Ltd., London, pp. 1-45.

Rostoker W., Lereim P., Galante J.O., (1979). Effect of an in vivo environment on the strength of bone cement. *Journal of Biomedical Materials Research*, Vol. 13, pp. 365-370.

Saha S., Pal S., (1984). Mechanical properties of bone cement : a review. *Journal of Biomedical Materials Research*, Vol. 18, pp. 435-462.

Scheerer E.W., Swartz M.L., Norman R.D., Phillips R.W., (1964). Residual monomer of restorative resins. *Journal of Dental Research*, Vol. 43, pp.672-677.

Schoenfeld C.M., Conard G.J., Lautenschlager E.P., (1979). Monomer release from methacrylate bone cement during simulated in vivo polymerisation.

Sih G.C., Berman A.T., (1980). Fracture toughness concept applied to methylmethacrylate. *Journal of Biomedical Materials Research*, Vol. 14, pp. 311-324.

Sih G.C., Matic P., Berman A.T., (1981). Failure prediction of the total hip prosthesis system. *Journal of Biomechanics*, Vol. 14, pp. 833-841.

Smith D.C., (1958). Fracture markings in polymethylmethacrylate. *Nature*, Vol. 182, pp. 132-133.

Smith D.C., (1961). The acrylic denture base. *British Dental Journal*, Vol. 111, pp. 9-17.

Smith D.C., (1971). Medical and dental applications of cements. *Journal of Biomedical Materials Research Symposium*, Vol. 1, pp. 189-205.

Smith D.C., Bains M.E.D., (1956). The detection and estimation of residual monomer in polymethylmethacrylate. *Journal of Dental Research*, Vol. 35, pp. 16-24.

Smith R.M., (1988). Gas and Liquid Chromatography in Analytical Chemistry, John Wiley and Sons, Chichester, pp. 1-17.

Stark C.F., (1979). Fracture and fatigue characteristics of bone cements. *Journal of Biomedical Materials Research*, Vol. 13, pp. 339-342.

Stauffer R.N., (1982). Ten-year follow-up study of total hip replacement. *Journal of Bone and Joint Surgery*, Vol. 64-A, pp. 983-990.

Struik L.C.E., (1978). Physical Aging in Amorphous Polymers and Other Materials, Elsevier Scientific Publishing Company, Amsterdam.

Tattersall H.G., Tappin G., (1966). The work of fracture and its measurement in metals, ceramics and other materials. *Journal of Materials Science*, Vol. 1, pp. 296-301.

Turner C.E., (1973). Fracture toughness and specific fracture energy : A re-analysis of results. *Materials Science and Engineering*, Vol. 11, pp. 275-282.

Topoleski L.D.T., Ducheyne P., Cuckler J.M., (1990). A fractographic analysis of in vivo poly(methylmethacrylate) bone cement failure mechanisms. *Journal of Biomedical Materials Research*, Vol. 24, pp. 135-154.

Topoleski L.D.T., Ducheyne P., Cuckler J.M., (1992). The fracture toughness of titanium-fiber-reinforced bone cement. *Journal of Biomedical Materials Research*, Vol. 26, pp. 1599-1617.

Venz S., Dickens B., (1991). NIR-spectroscopic investigation of water sorption characteristics of dental resins and composites. *Journal of Biomedical Materials Research*, Vol. 25, pp. 1231-1248.

Wang C.T., Pilliar R.M., (1989a). Fracture toughness of acrylic bone cements. *Journal of Materials Science*, Vol. 24, pp. 3725-3738.

Wang C.T., Pilliar R.M., (1989b). Bone cement bonding - interfacial fracture toughness determination. *Clinical Materials*, Vol. 4, pp. 135-153.

Waters, (1975). Know more about your polymer, Company Literature, Walters, Division of Millipore, USA.

Watson M.B., Miles A.W., Clift S.E., (1990). The influence of curing time and environment on the fracture properties of bone cement. *Clinical Materials*, Vol. 6, pp. 299-305.

Weber F.A., Charnley J., (1975). A radiological study of fractures of acrylic cement in relation to the stem of a femoral head prosthesis. *Journal of Bone and Joint Surgery*, Vol. 57-B, pp. 297-301.

Wiklund I., Romanus B., (1991). A comparison of quality of life before and after arthroplasty in patients who had arthrosis of the hip joint. *Journal of Bone and Joint Surgery*, Vol. 73-A, pp. 765-769.

Willert H.G., Bertram H. and Buchhorn G.H., (1990). Osteolysis in Alloarthroplasty of the Hip. *Clinical Orthopaedics and Related Research*, Vol. 258, pp. 108-121.

Willert H.G., Frech H.A., Bechtel A., (1975). Measurements of the quantity of monomer leaching out of acrylic bone cement into the surrounding tissues during the process of polymerisation. In "Biomedical Applications of Polymers", Gregor H.P. (ed.), Plenum Press, New York, pp. 121-133.

Wright T.M., Robinson R.P., (1982). Fatigue crack propagation in polymethylmethacrylate bone cements. *Journal of Materials Science*, Vol. 17, pp. 2463-2468.

Wright T.M., Sullivan D.J., Arnoczky S.P., (1984). The effect of antibiotic additions on the fracture properties of bone cements. *Acta. Orthop.Scand.*, Vol. 55, pp. 414-418.

Wroblewski B.M., (1977). Leaching out from acrylic bone cement experimental evaluation. *Clinical Orthopaedics and Related Research*, Vol. 124, pp. 311-312.

APPENDIX A

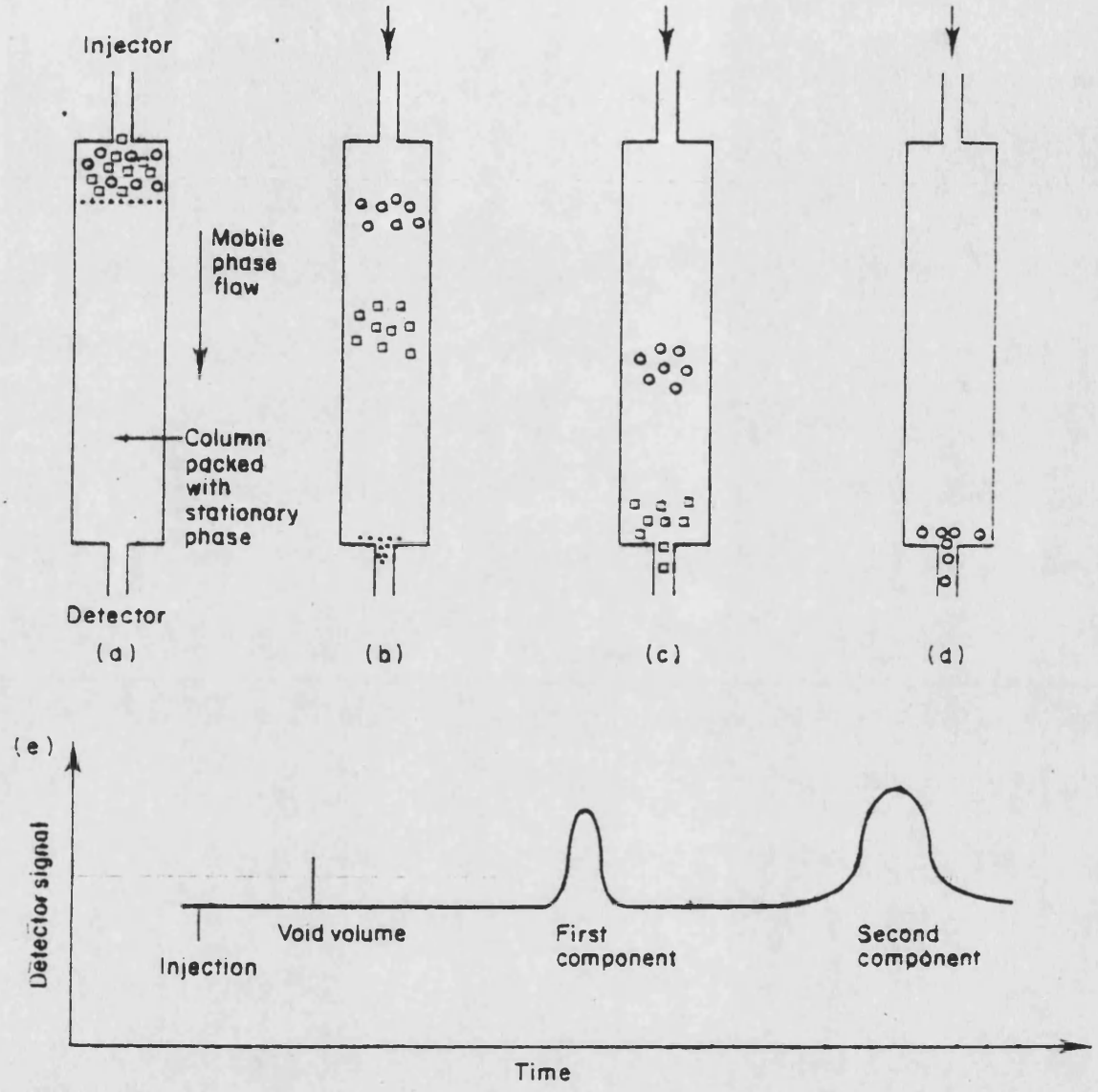
GAS CHROMATOGRAPHY AND GEL PERMEATION CHROMATOGRAPHY

A.1 Gas Chromatography (GC) Technique

Chromatography essentially involves the separation of two or more compounds from a mixture. The compounds are first dissolved in a solvent, a sample of which is injected into the chromatograph. The sample is then carried through the column by a carrier gas. The column is packed with a stationary phase for which the components to be separated have differing affinities. As the sample proceeds through the column, the individual components interact with the stationary phase to varying degrees (Christian and O'Reilly, 1986). Thus their passage through the column is slowed to different degrees, as shown in Figure A.1. As the sample leaves the column it passes through a detector capable of indicating the presence of the components. The output from the detector is fed to a chart recorder and the graph produced is called the chromatogram (Heftmann, 1967).

A.2 Gel Permeation Chromatography (GPC) Technique

Gel permeation chromatography is a term used to describe the sieving action of molecular size separation on a gel column (Huggett, Bates and Packham, 1983). The chemically inert gel column contains a controlled wide distribution of pores sizes to separate the specimen into varying molecular sizes. The sample to be evaluated is dissolved in a solvent, a sample of which is then injected into GPC equipment. The larger molecules of the dissolved material are least able to pass through the pores and are thus rapidly passed through the column. The smaller molecules penetrate more of the pores and are thus retained in the column for a longer period, as shown in Figure A.2 (Jagger, 1978). The concentration of the dissolved material in the carrier solvent is measured by a detector as it exits the column, and is recorded on a chromatogram.



Chromatographic separation on a column. (a) Introduction of the sample. (b) Elution of unretained components at column void volume. (c) Elution of more weakly retained compound. (d) Elution of more strongly retained component. (e) Chromatogram recorded by detector at end of the column.

Figure A.1 : Schematic Diagram of a Gas Chromatograph.

(After Smith, 1988)

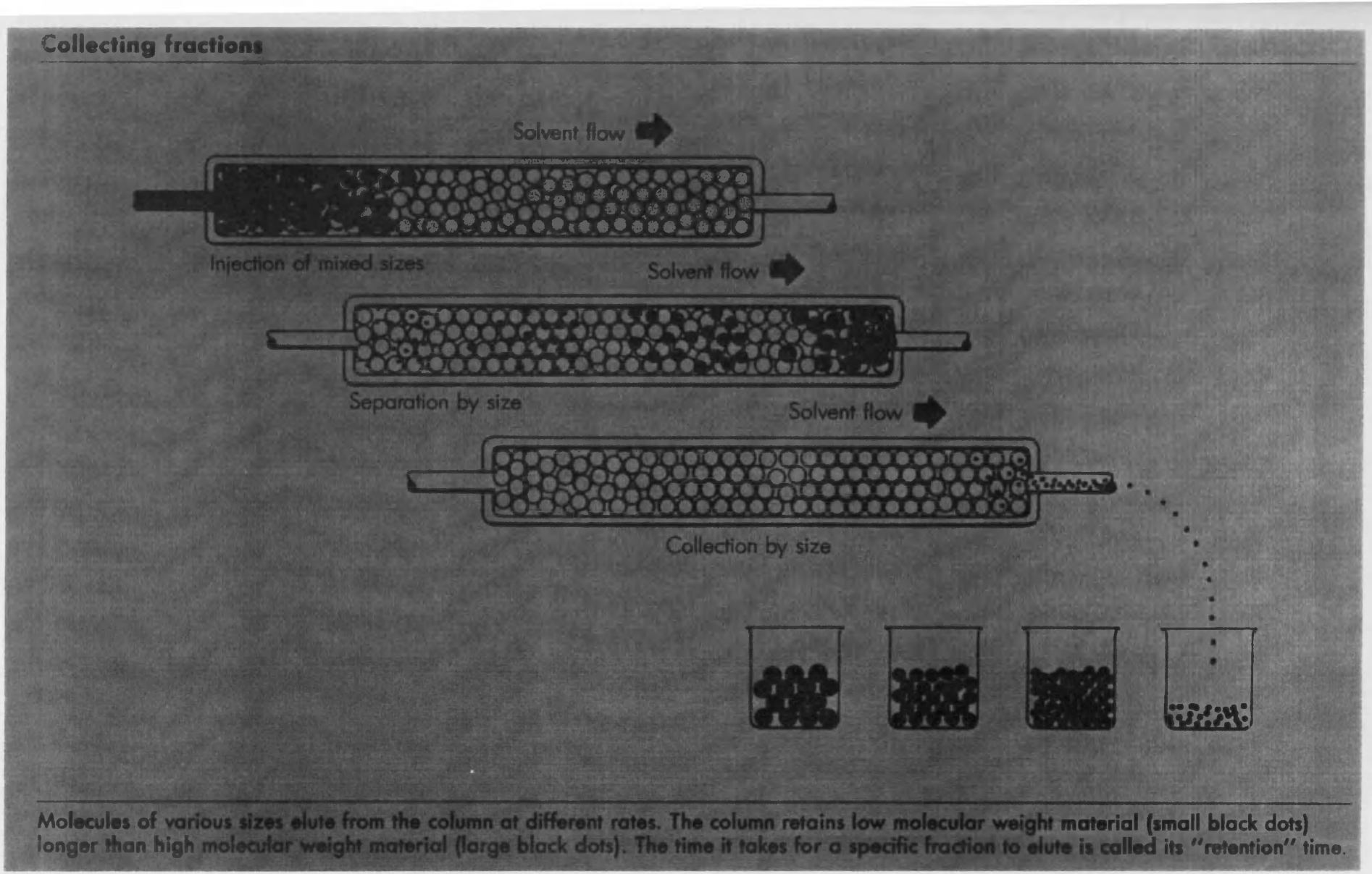


Figure A.2 : Schematic Diagram of a Gel Permeation Chromatograph. (After Waters, 1975)

APPENDIX B

SOLUBILITY OF METHYLMETHACRYLATE IN WATER

B.1 Solubility Limits

The solubility of methylmethacrylate in water is very low (Schoenfeld, Conard, and Lautenschlager, 1979). Smith and Bains (1956) reported values of 1.59% for the solubility of methylmethacrylate monomer in water at 20°C and 1.50% at 30°C. Linder, Harthon and Kullberg (1976) supported this value, reporting a saturation concentration of "25 x 600 micrograms" of monomer per millilitre of water at 20°C, which equates to 1.6ml monomer in 100ml water, a solubility limit of 1.6%.

B.1.1 Evaluation of the Amount of Monomer which Leached into the Water Based Storage Media

Taking storage of samples at 21°C as an example, the solubility limit of methylmethacrylate monomer in water is approximately 1.6%. The bone cement samples used in this thesis were stored in glass jars containing 1.5 litres of water, therefore up to 24ml of monomer would have been capable of being dissolved in the water. Each glass jar contained 32 samples, weighing approximately 2 grams each, which gave a total weight of 64 grams of cement in each jar. The cement contained approximately 2.2% residual monomer when first placed in the water, hence there was a total of approximately 1.4 grams of residual monomer which could have been leached into the 1.5 litres of water. The weight of 1ml of methylmethacrylate at 20°C is approximately 0.94 grams, thus there was a total of 1.5ml of residual monomer available to be leached into the storage water. This was well below the saturation concentration of 24ml of monomer in 1.5 litres of water, so theoretically the volume of water used to store the samples was capable of leaching all the monomer from the cement samples.

APPENDIX C

STATISTICAL RESULTS

C.1 Introduction

The level of statistical significance of the trends identified from the experimental results was evaluated by use of 95% confidence intervals (95%CI). The effects of the different storage conditions on the fracture behaviour, environmental ingress, residual monomer content and molecular mass of the bone cement were compared by plotting the 95%CI (given in the tables of results) for two different environments on the same graph. The effect of storing samples at body temperature as opposed to laboratory temperature was evaluated for the four different storage media, and the effects of storage in air, Ringer's, and lipid were compared with the effect of storage in water at each of the two temperatures. the term "significant" is used to describe a statistical significance. For example, if the 95%CI do not overlap for the two environments then there is a significant difference between those two environments.

The formula for calculating the 95% confidence intervals is given below:

$$95\%CI = \bar{x} \pm t_{0.05}\,(n-1)\,s/\sqrt{n}$$

where ; $\bar{x}$ = mean value

n = number of samples

s = standard deviation

$t_{0.05}$ refers to the Students t-distribution at the 95% level of significance

The following graphs show the 95%CIs for all the results in this thesis.

Figure C.1 : 95%CI for WOF Tests on Normal Cement in Air

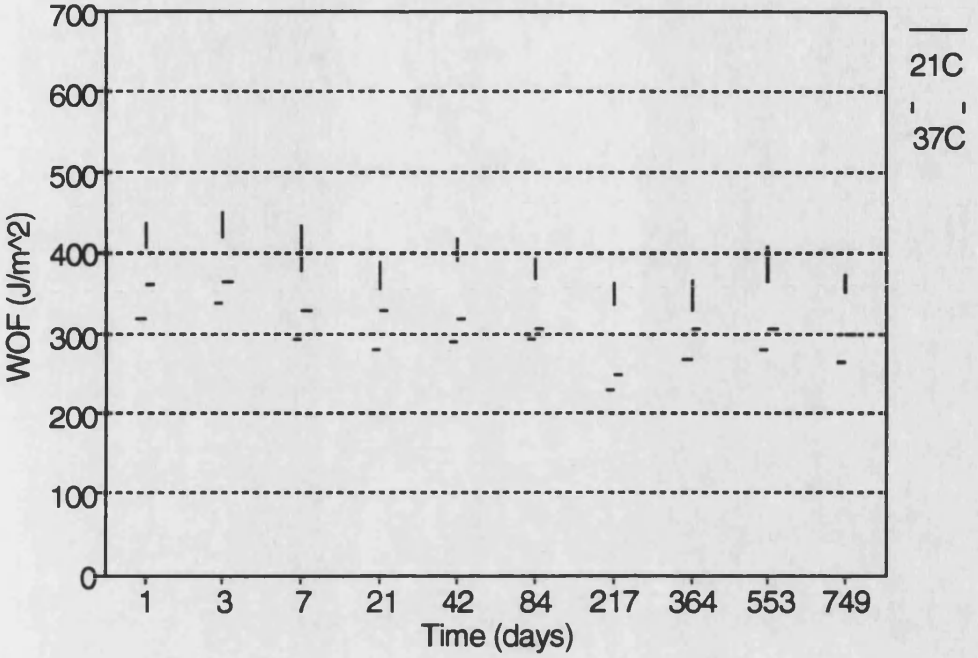


Figure C.2 : 95%CI for WOF Tests on Normal Cement in Water

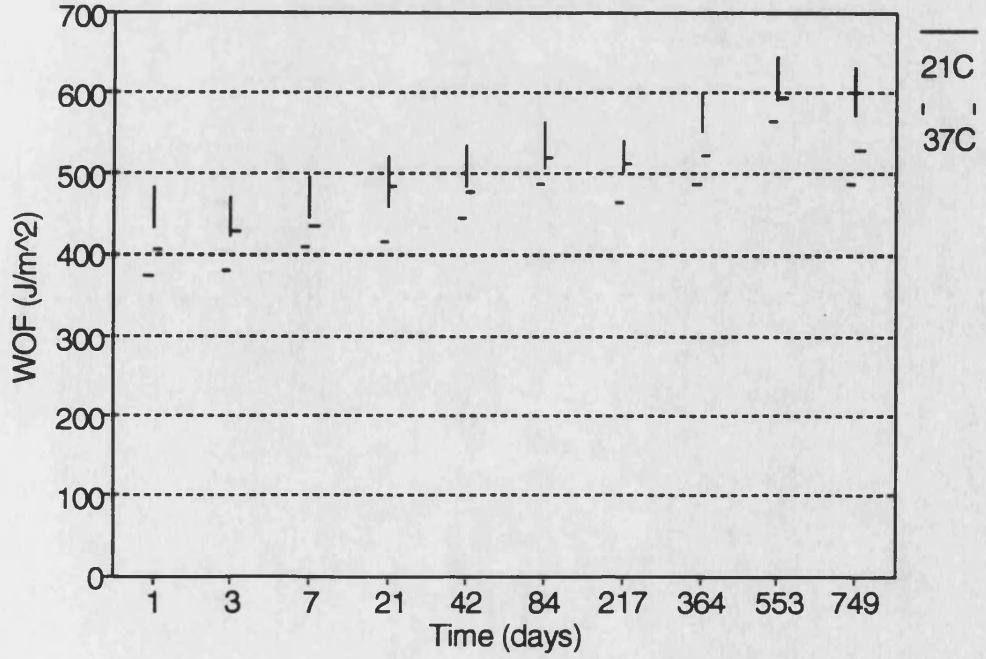


Figure C.3 : 95%CI for WOF Tests on Normal Cement in Ringer's

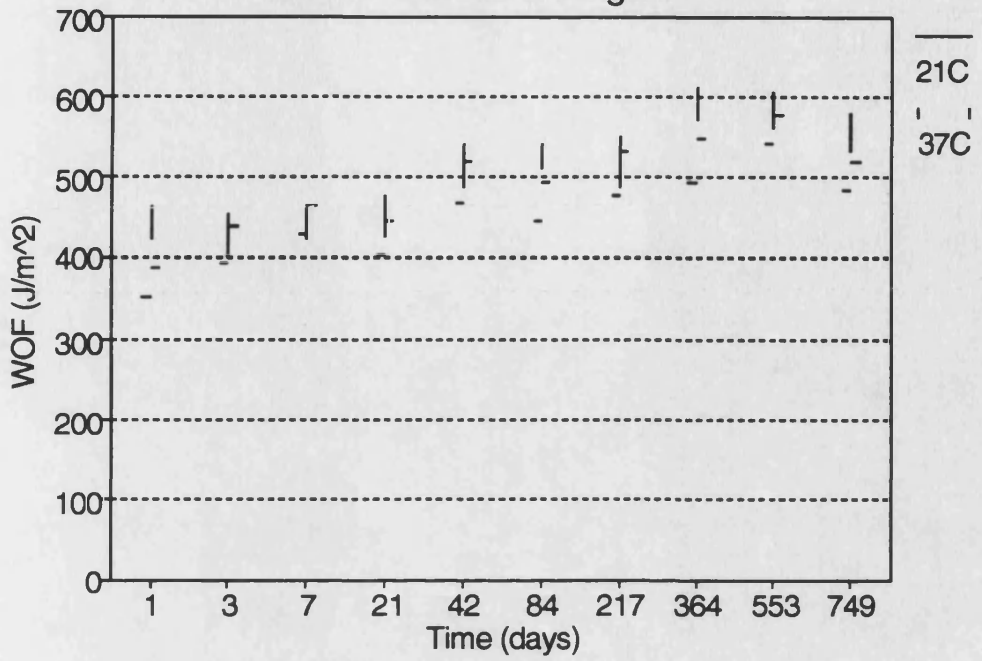


Figure C.4 : 95%CI for WOF Tests on Normal Cement in Lipid

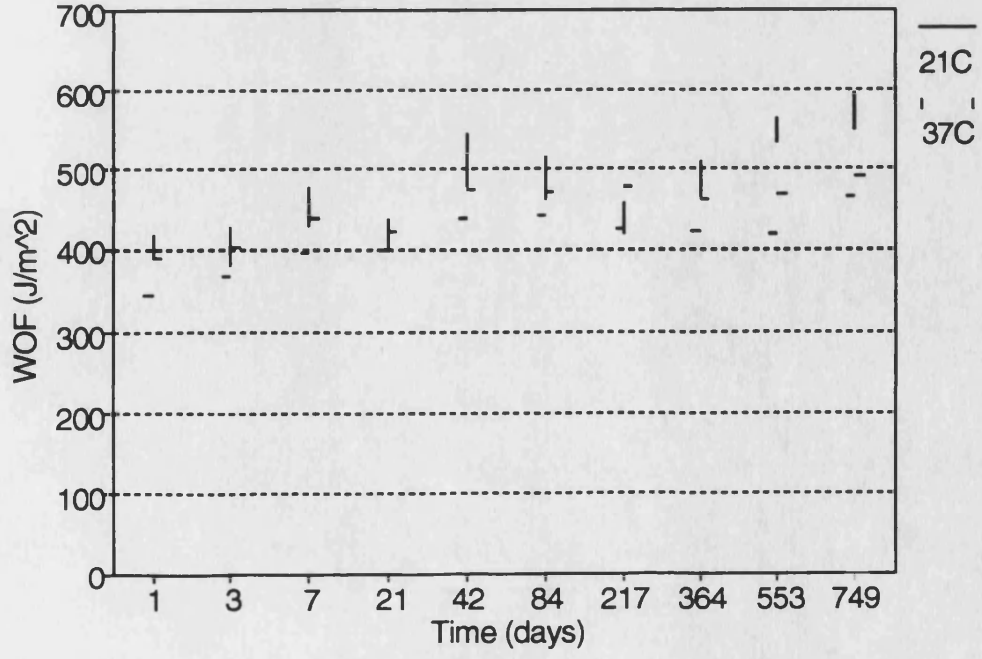


Figure C.5 : 95%CI for WOF Tests on Normal Cement at 21C

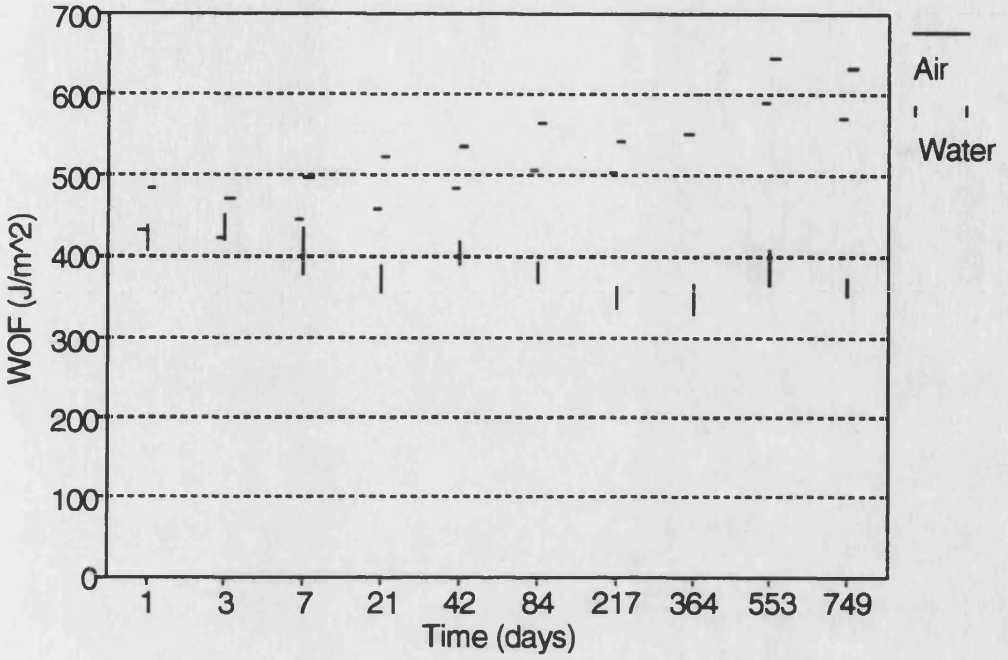


Figure C.6 : 95%CI for WOF Tests on Normal Cement at 37C

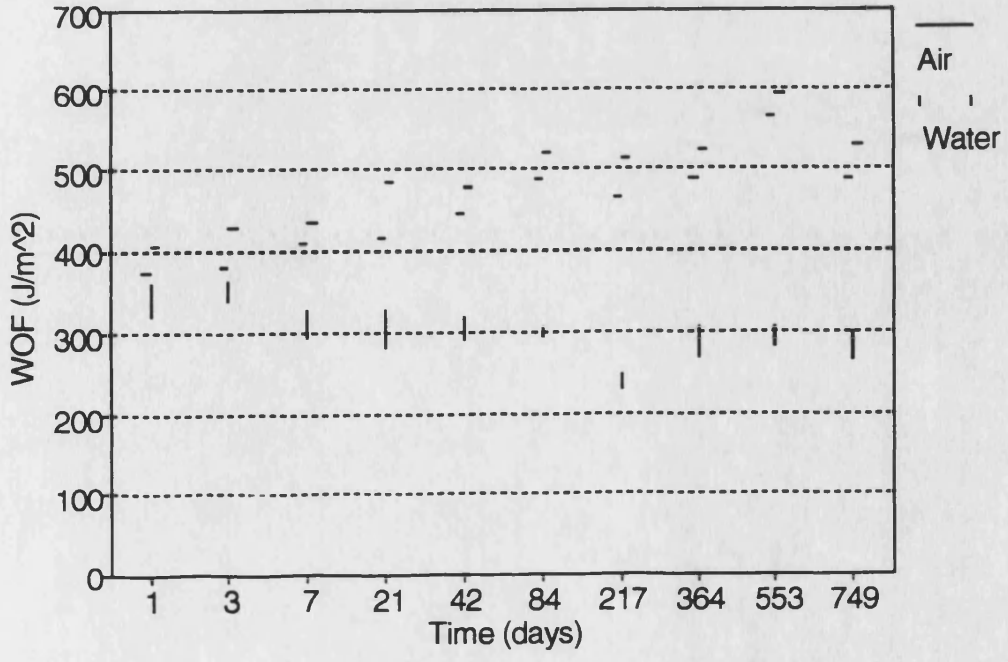


Figure C.7 : 95%CI for WOF Tests on Normal Cement at 21C

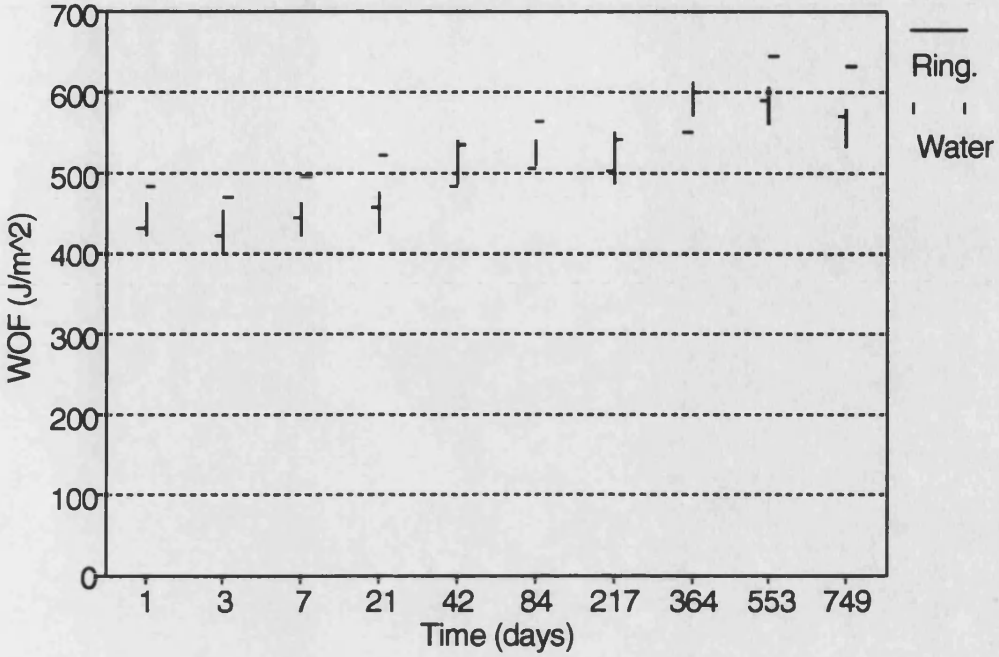


Figure C.8 : 95%CI for WOF Tests on Normal Cement at 37C

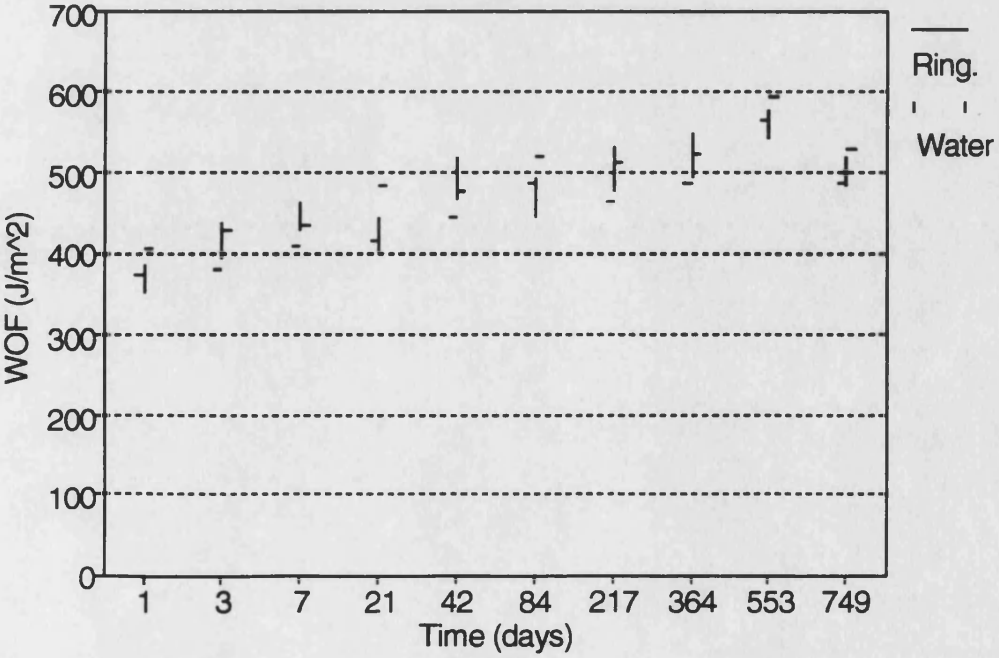


Figure C.9 : 95%CI for WOF Tests on Normal Cement at 21C

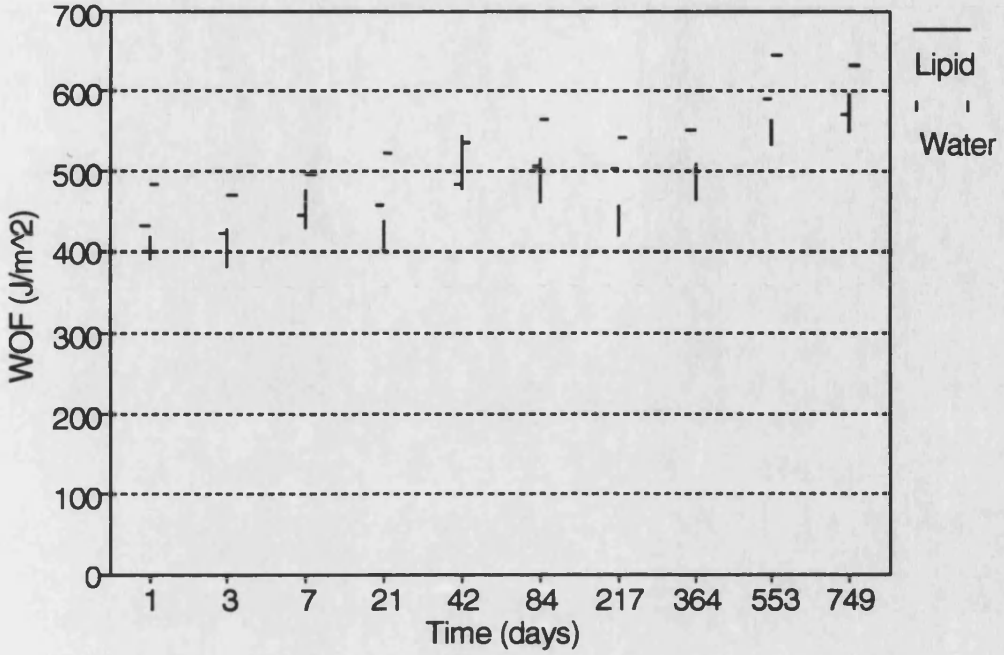


Figure C.10 : 95%CI for WOF Tests on Normal Cement at 37C

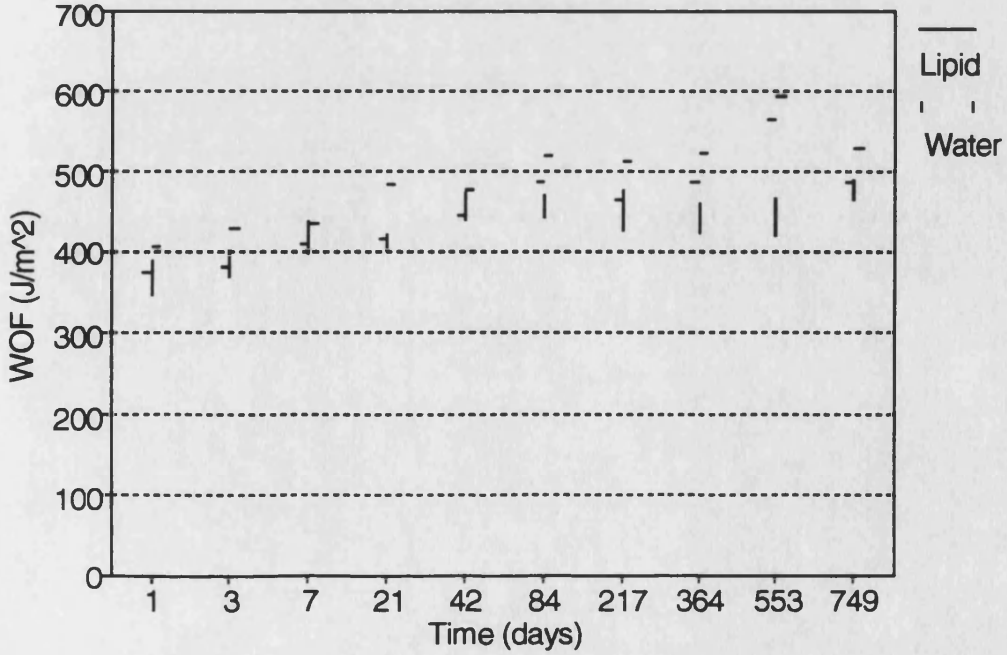


Figure C.11 : 95%CI for WOF Tests on Fully Cured Cement in Air

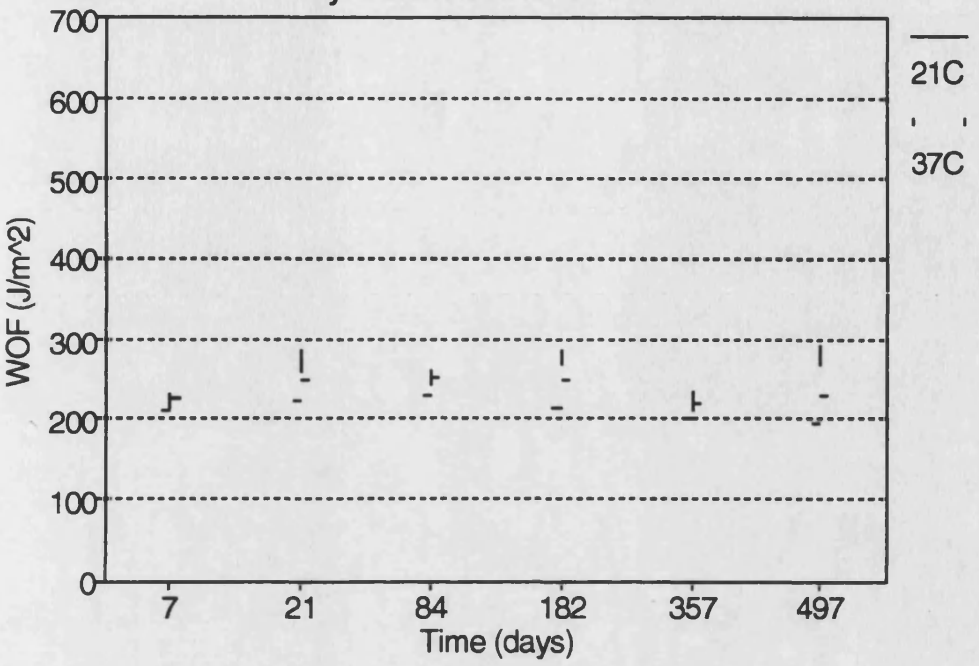


Figure C.12 : 95%CI for WOF Tests on Fully Cured Cement in Water

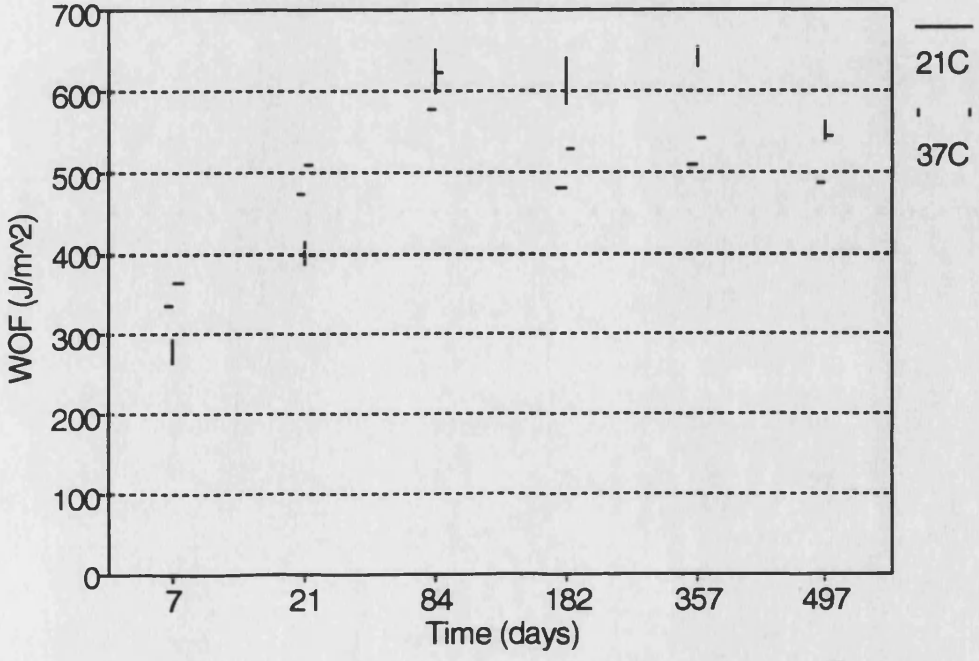


Figure C.13 : 95%CI for WOF Tests on Fully Cured Cement in Ringer's

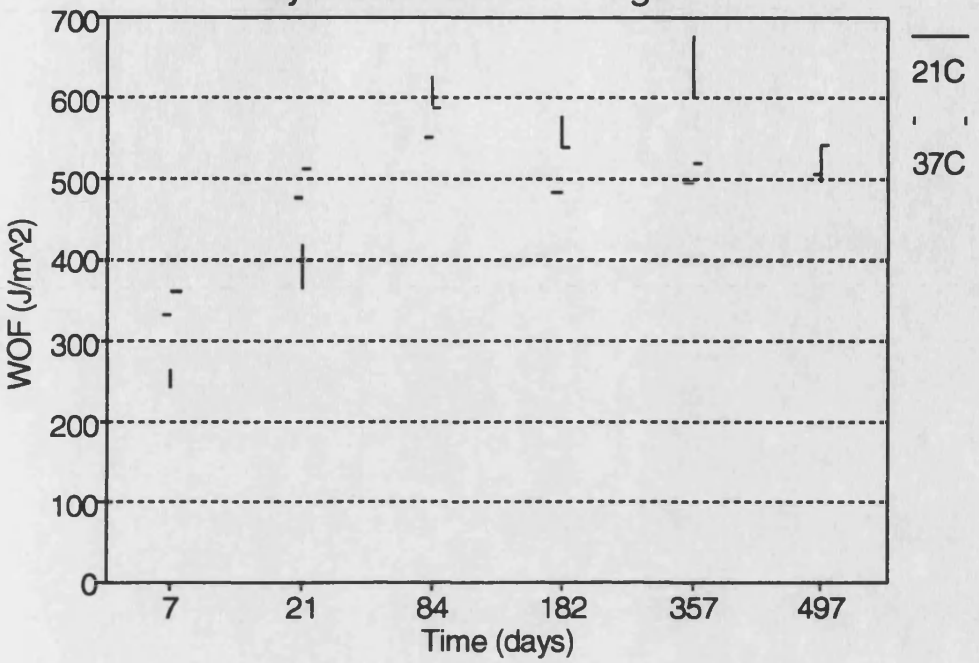


Figure C.14 : 95%CI for WOF Tests on Fully Cured Cement in Lipid

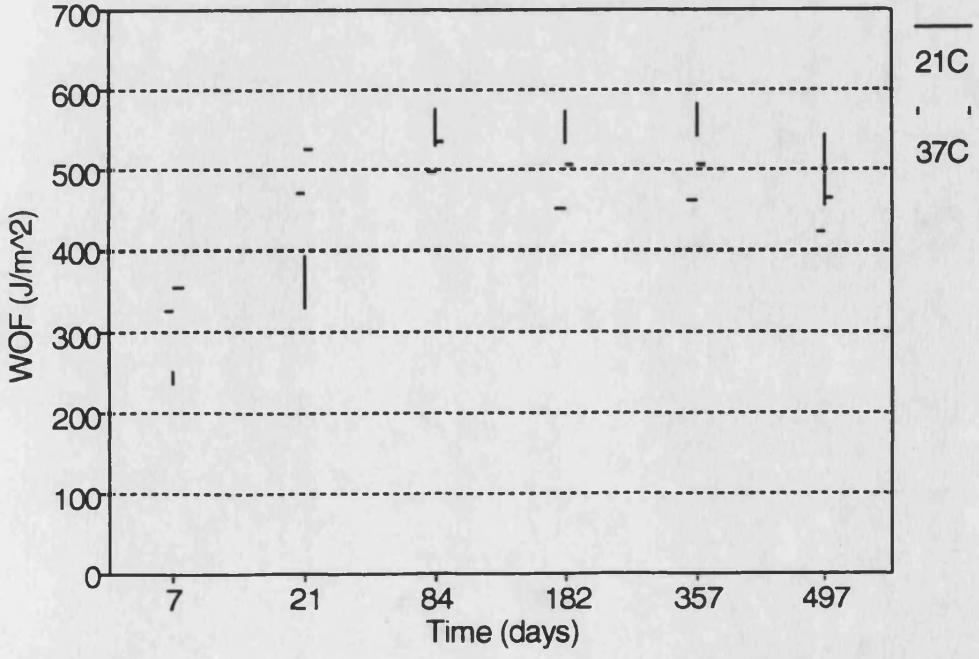


Figure C.15 : 95%CI for WOF Tests on Fully Cured Cement at 21C

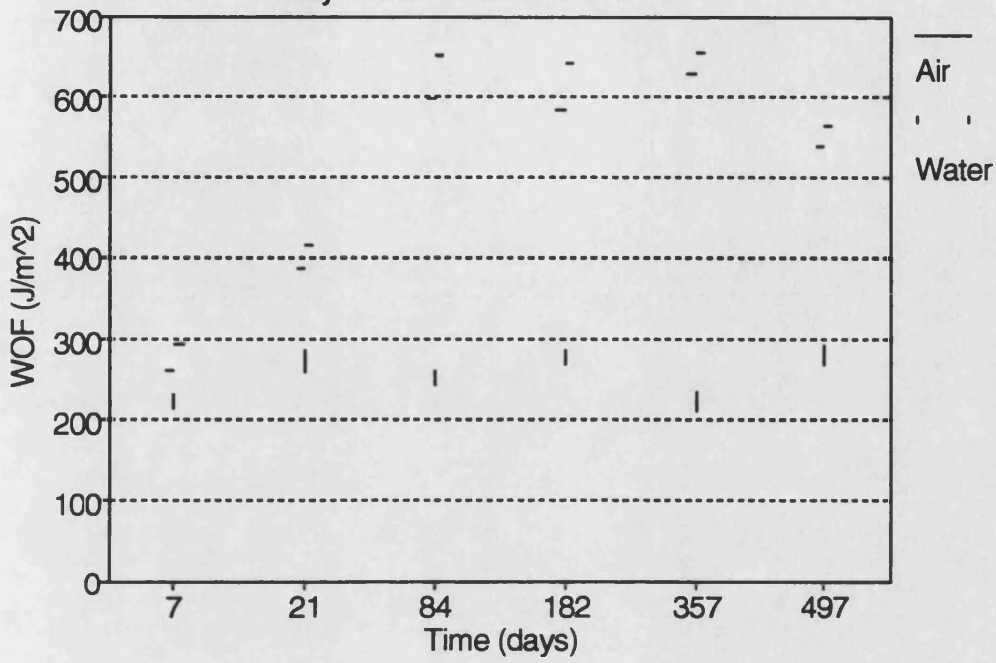


Figure C.16 : 95%CI for WOF Tests on Fully Cured Cement at 37C

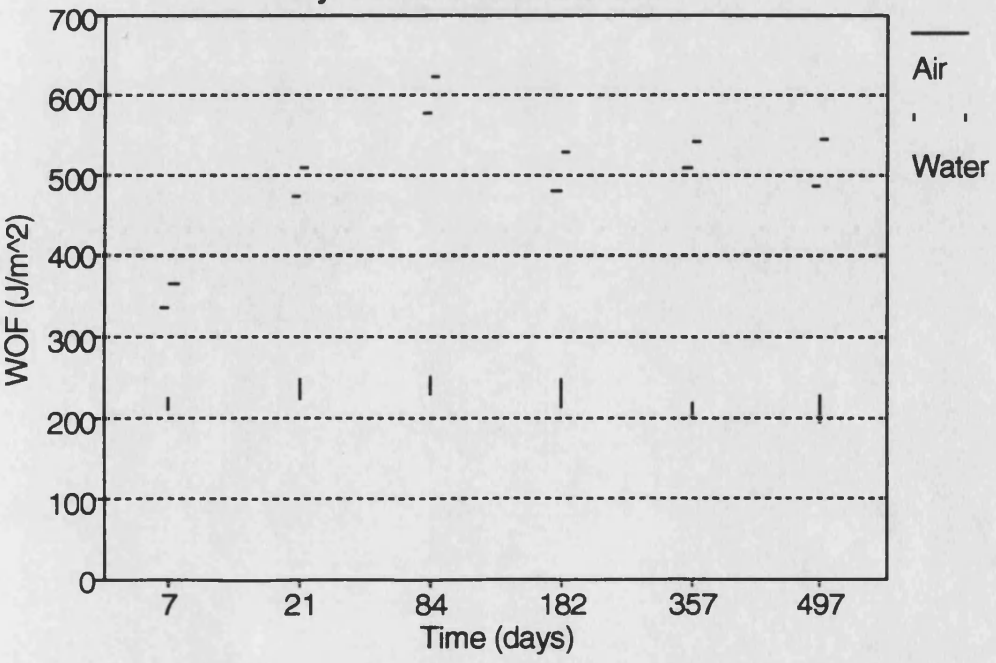


Figure C.17 : 95%CI for WOF Tests on Fully Cured Cement at 21C

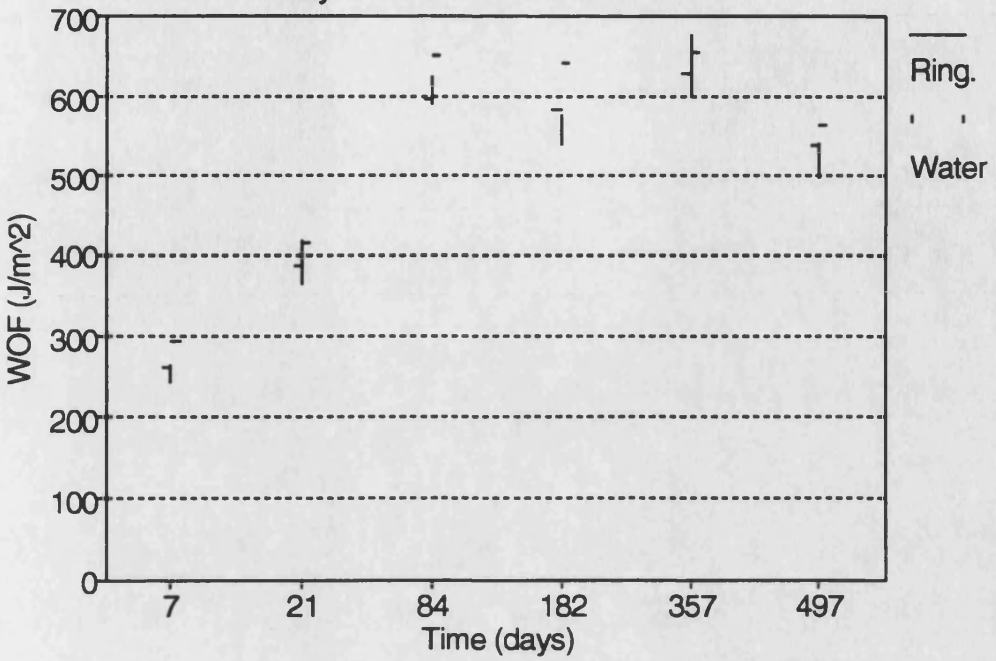


Figure C.18 : 95%CI for WOF Tests on Fully Cured Cement at 37C

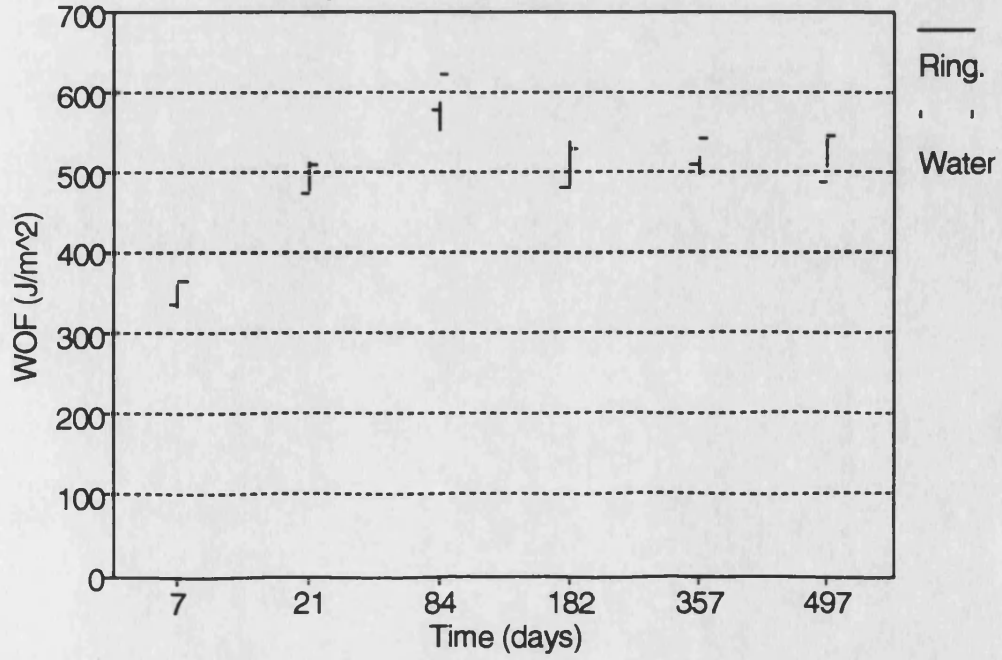


Figure C.19 : 95%CI for WOF Tests on
Fully Cured Cement at 21C

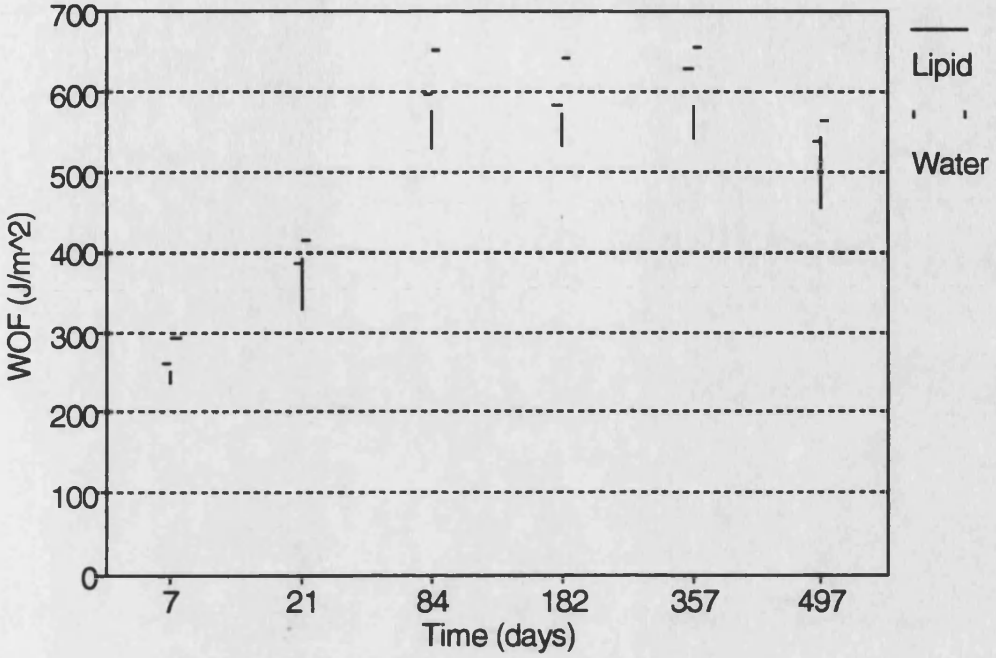


Figure C.20 : 95%CI for WOF Tests on
Fully Cured Cement at 37C

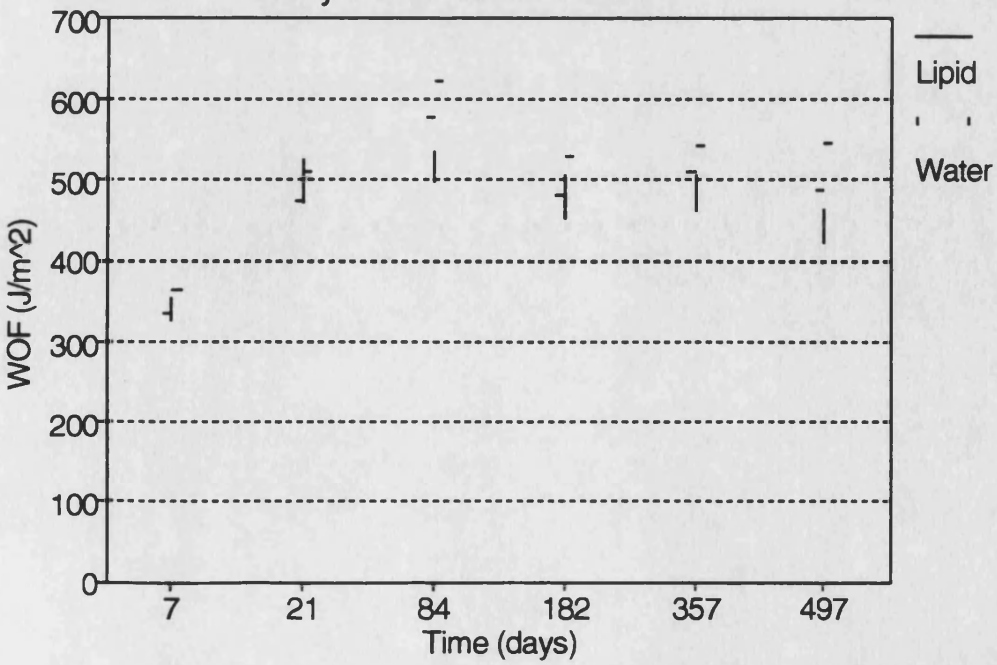


Figure C.21 : 95%CI for Rapid Fracture Tests on Normal Cement in Air

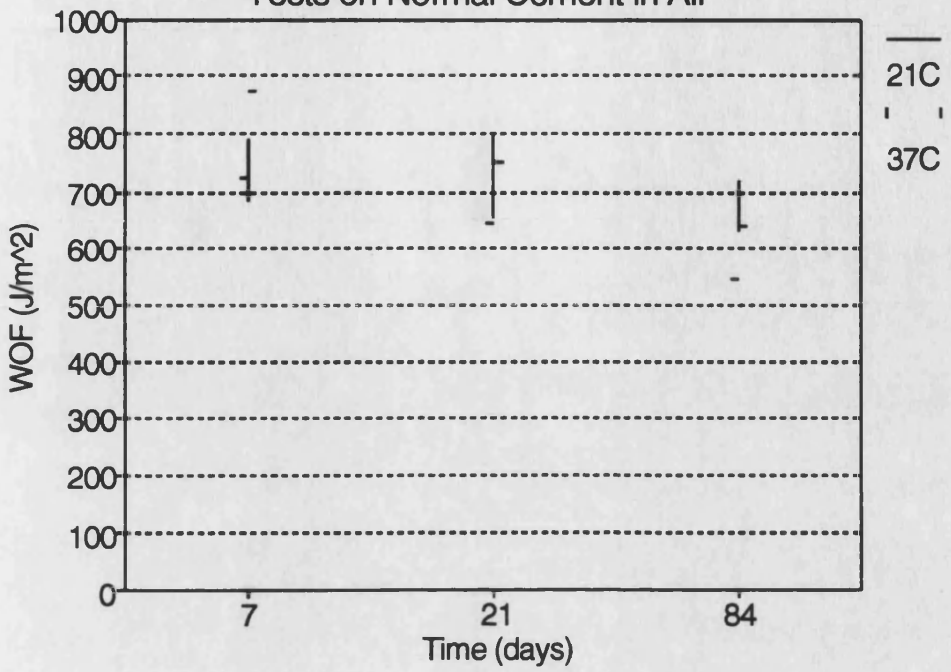


Figure C.22 : 95%CI for Rapid Fracture Tests on Normal Cement in Water

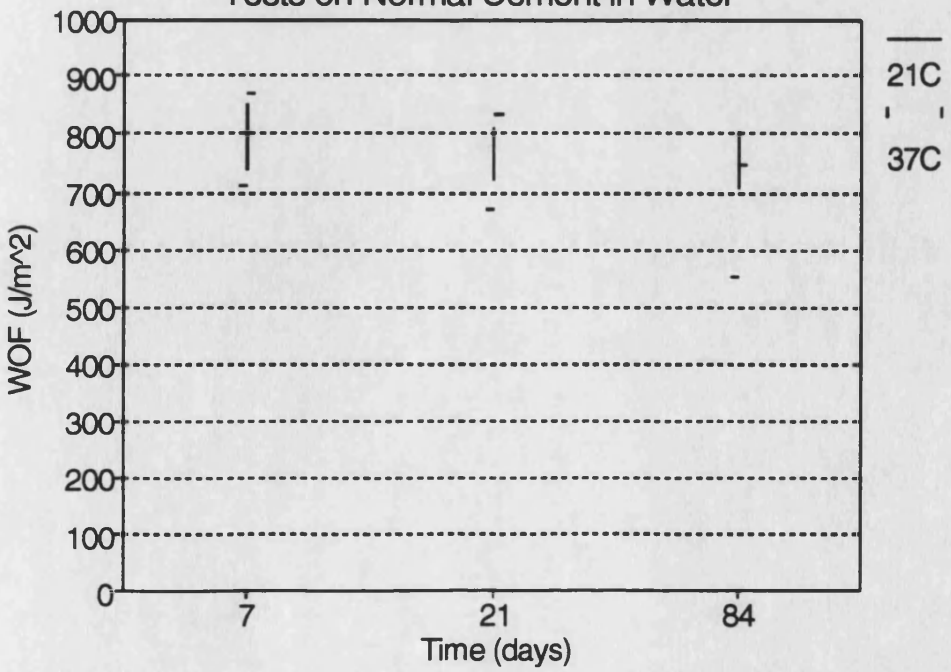


Figure C.23 : 95%CI for Rapid Fracture Tests on Normal Cement in Ringer's

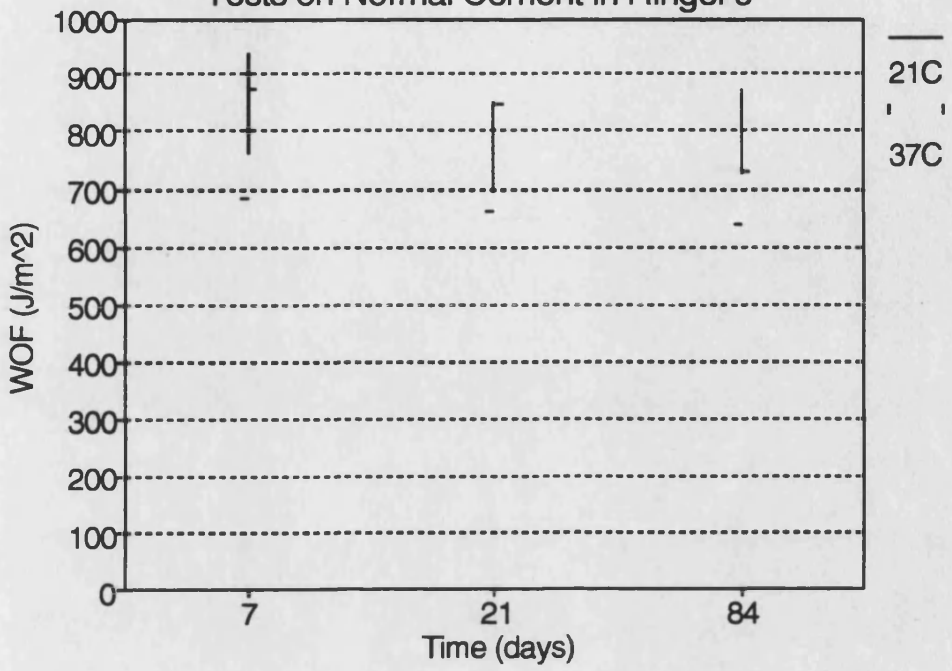


Figure C.24 : 95%CI for Rapid Fracture Tests on Normal Cement in Lipid

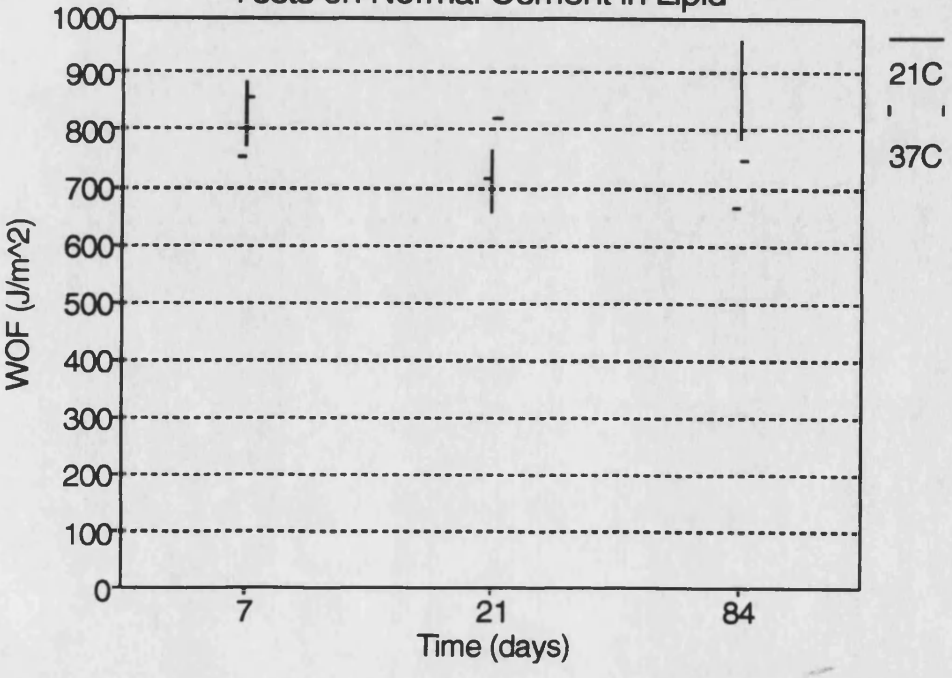


Figure C.25 : 95%CI for Rapid Fracture Tests on Normal Cement at 21C

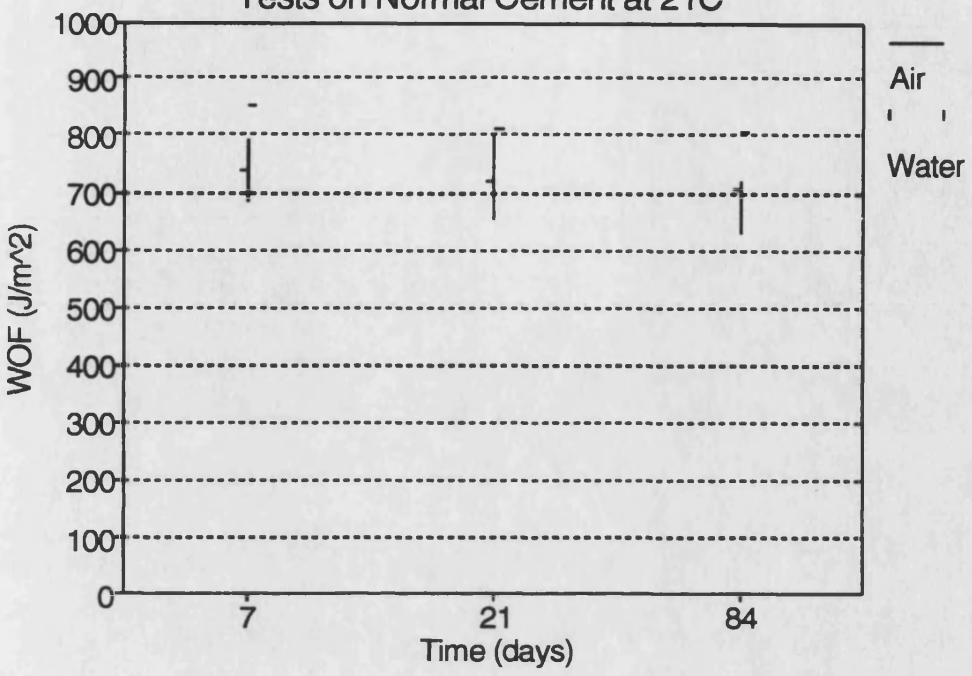


Figure C.26 : 95%CI for Rapid Fracture Tests on Normal Cement at 37C

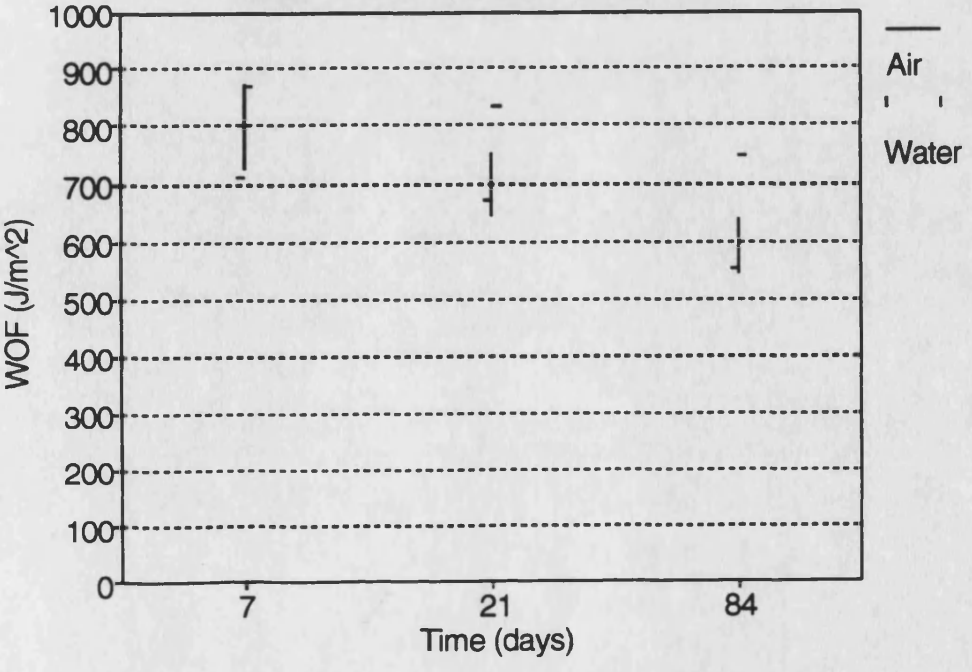


Figure C.27 : 95%CI for Rapid Fracture Tests on Normal Cement at 21C

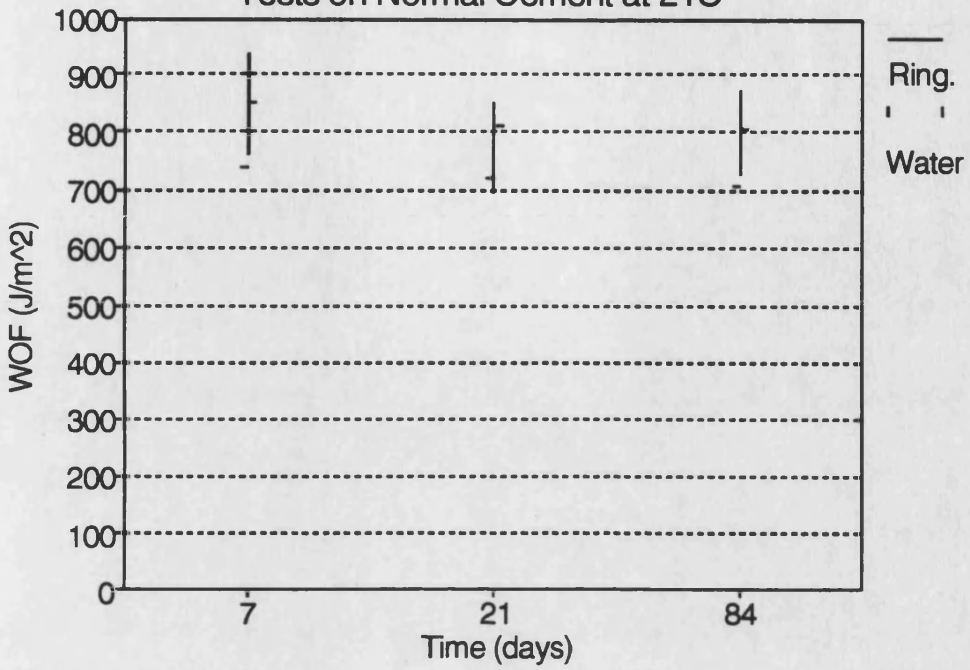


Figure C.28 : 95%CI for Rapid Fracture Tests on Normal Cement at 37C

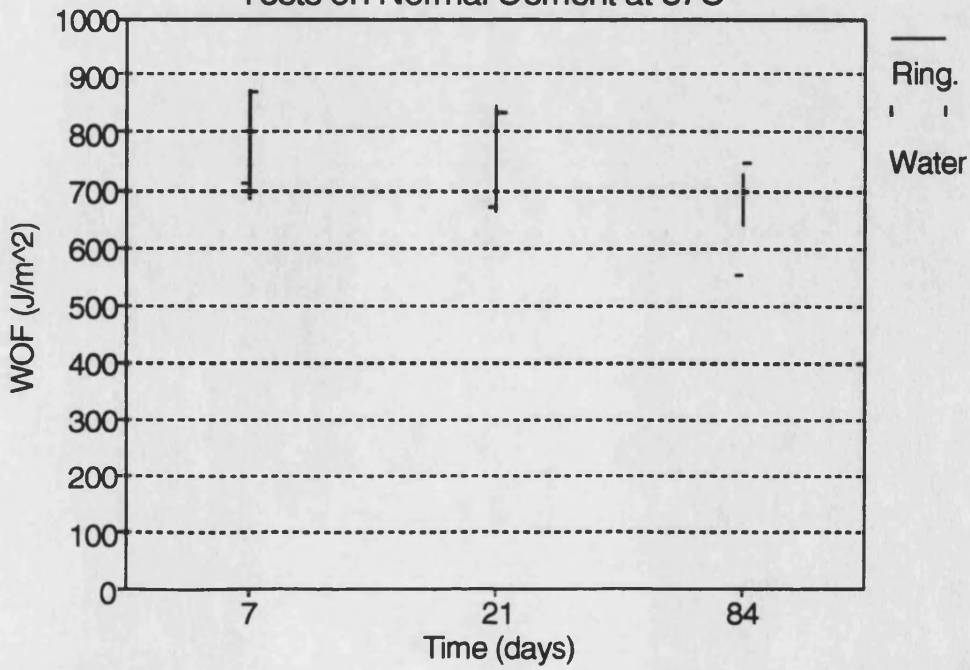


Figure C.29 : 95%CI for Rapid Fracture Tests on Normal Cement at 21C

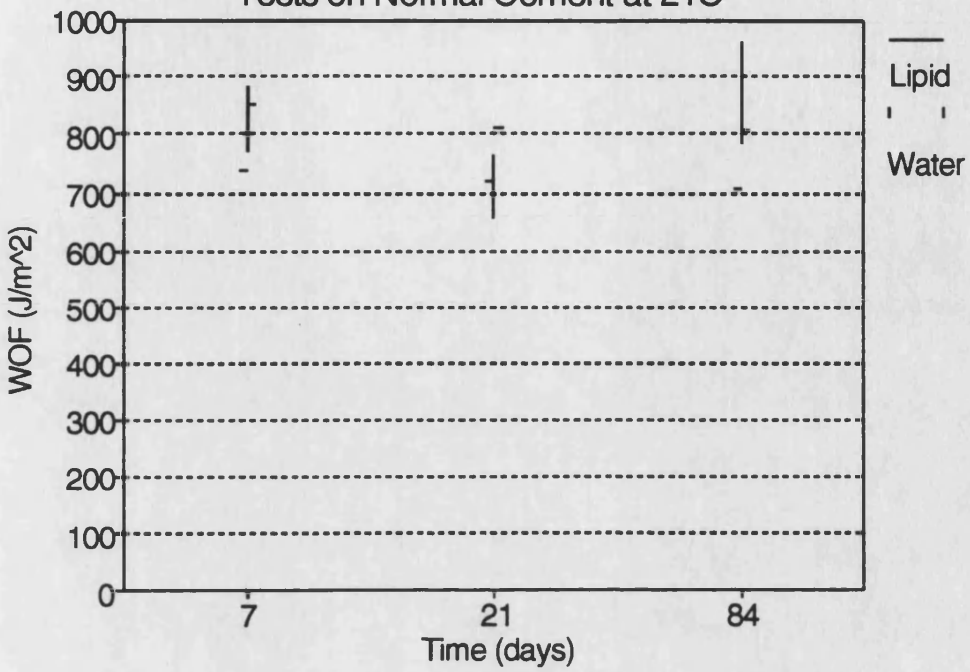


Figure C.30 : 95%CI for Rapid Fracture Tests on Normal Cement at 37C

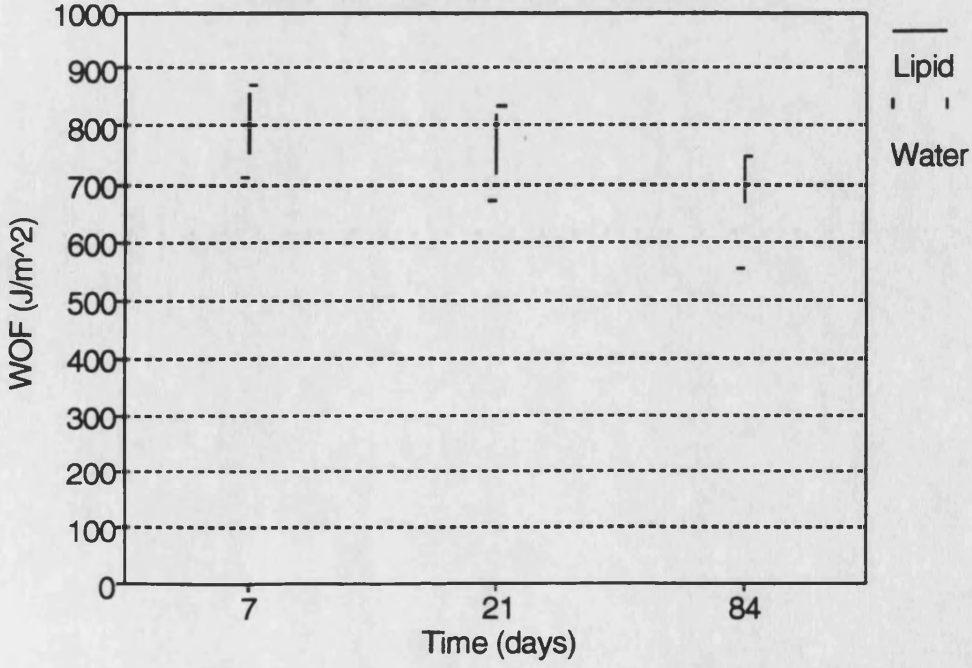


Figure C.31 : 95%CI for Ingress Results for Normal Cement in Air

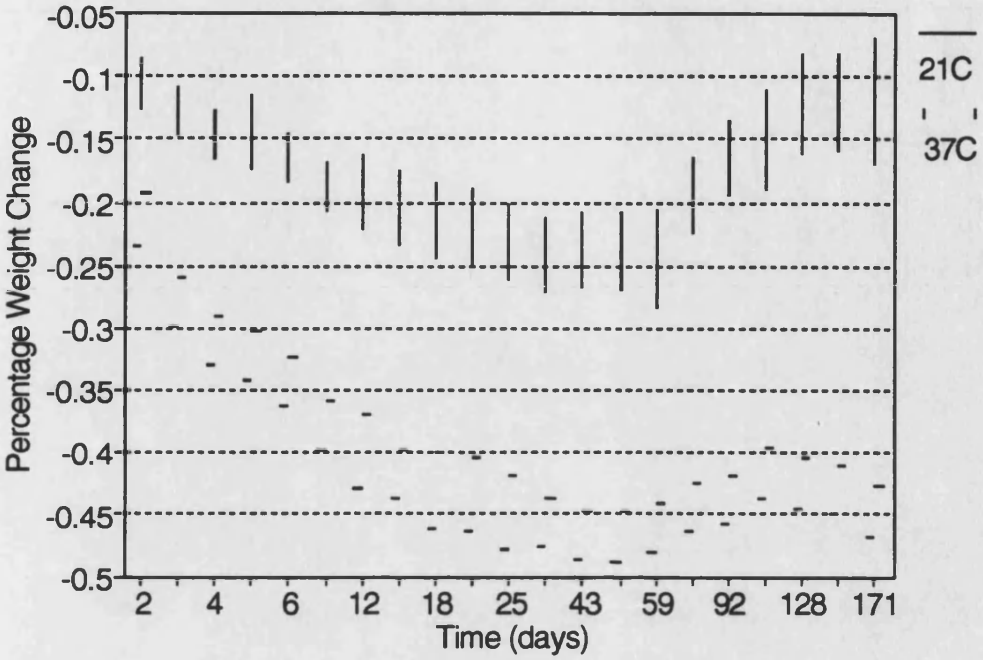


Figure C.32 : 95%CI for Ingress Results for Normal Cement in Water

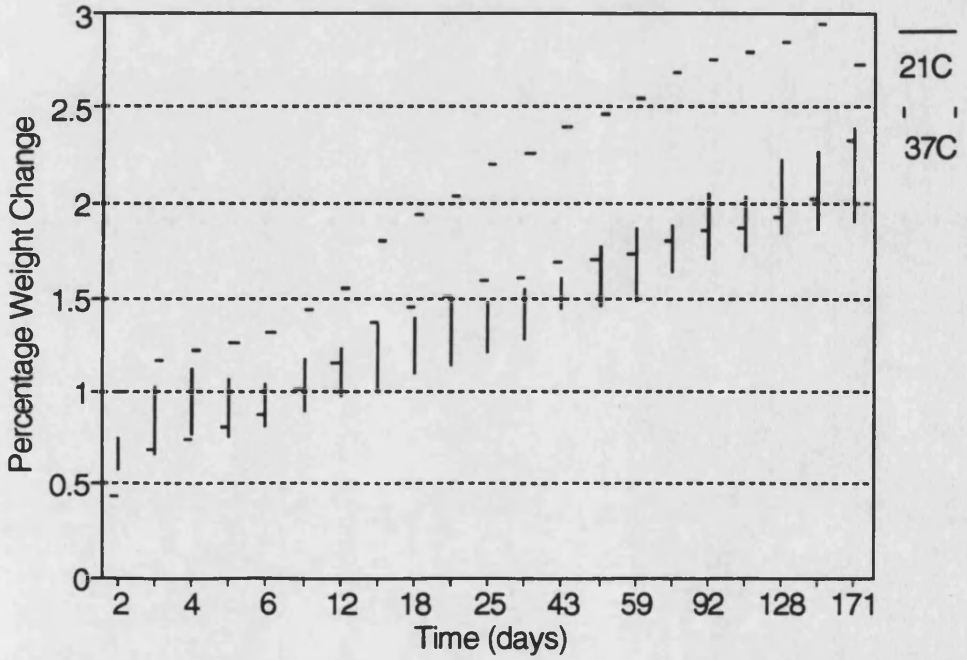


Figure C.33 : 95%CI for Ingress Results
for Normal Cement in Ringer's

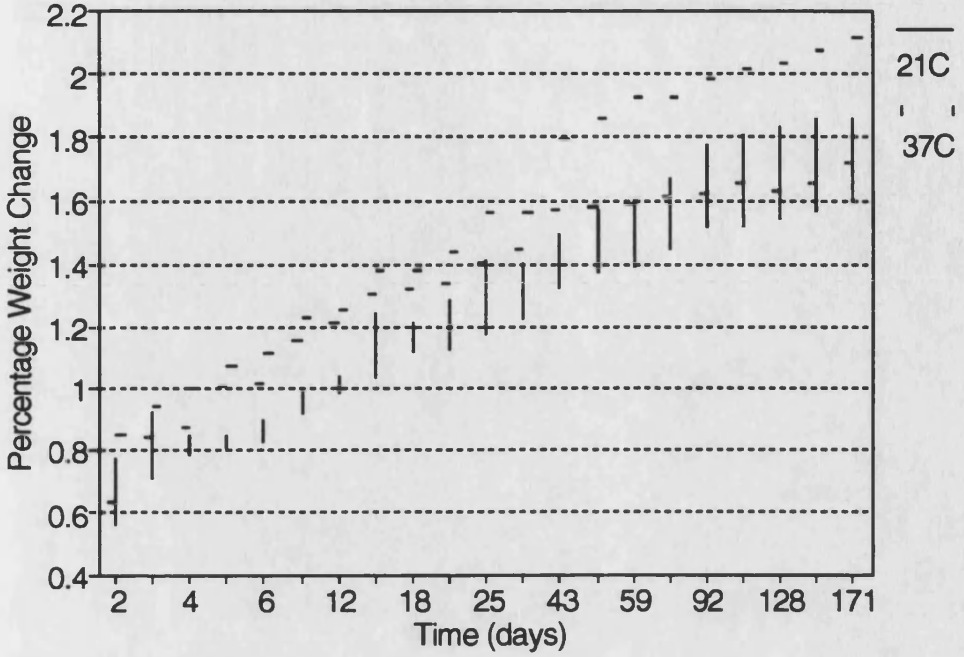


Figure C.34 : 95%CI for Ingress Results
for Normal Cement in Lipid

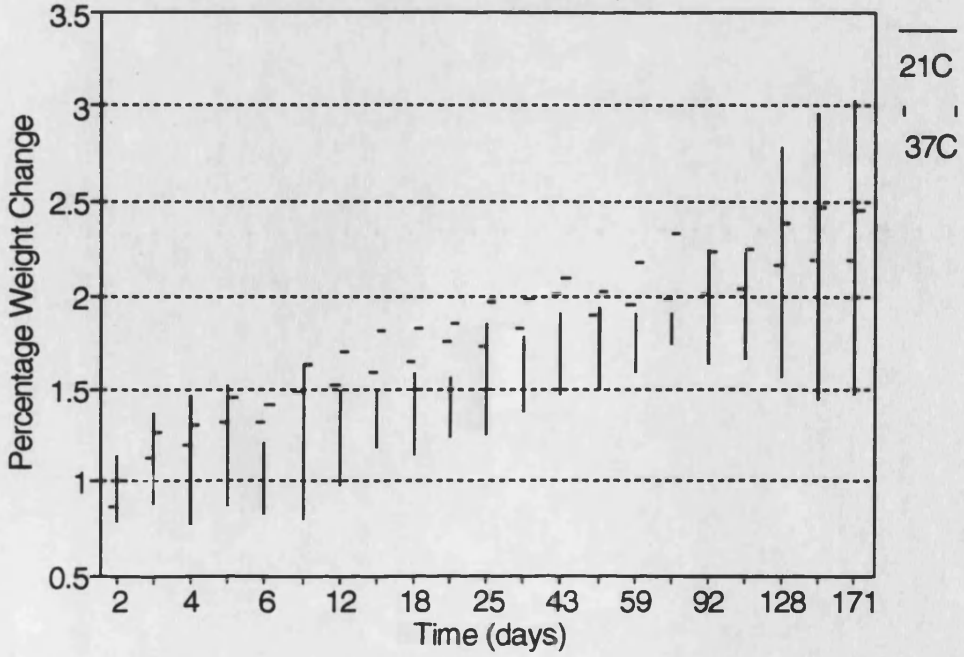


Figure C.35 : 95%CI for Ingress Results for Normal Cement at 21C

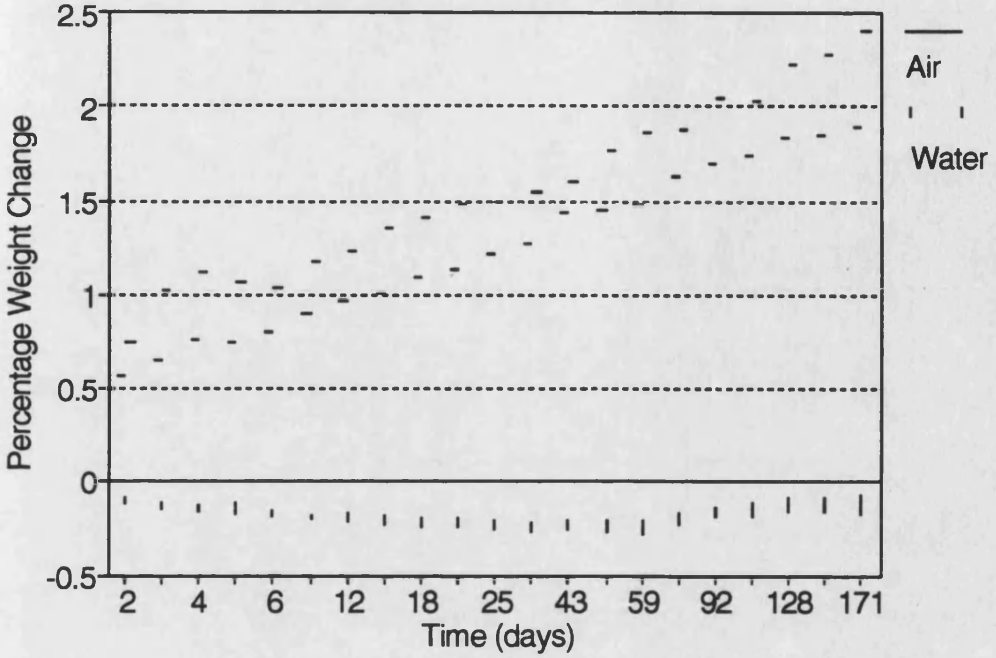


Figure C.36 : 95%CI for Ingress Results for Normal Cement at 37C

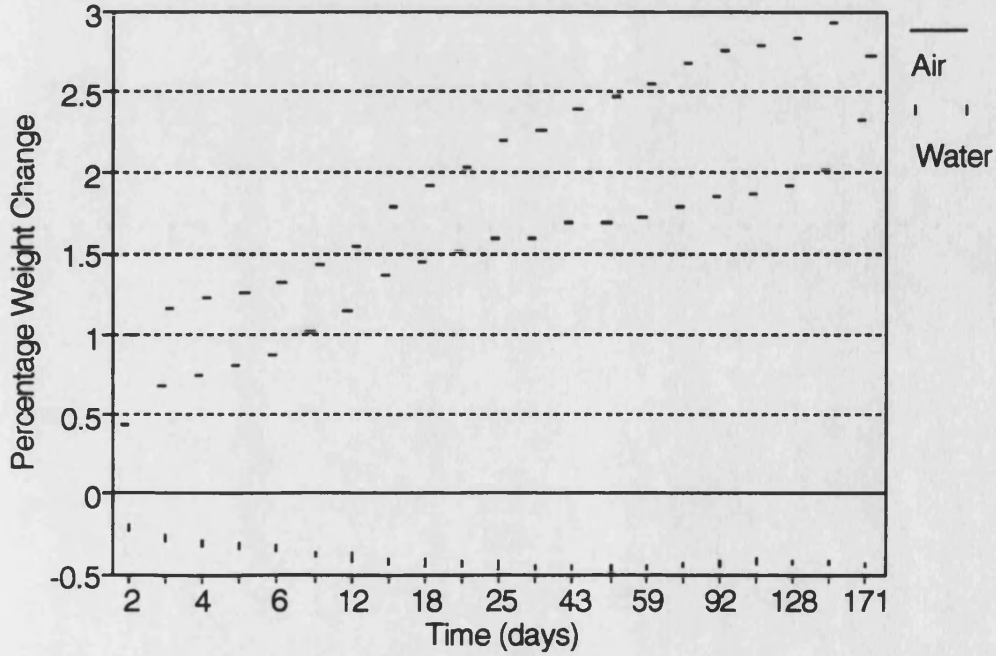


Figure C.37 : 95%CI for Ingress Results for Normal Cement at 21C

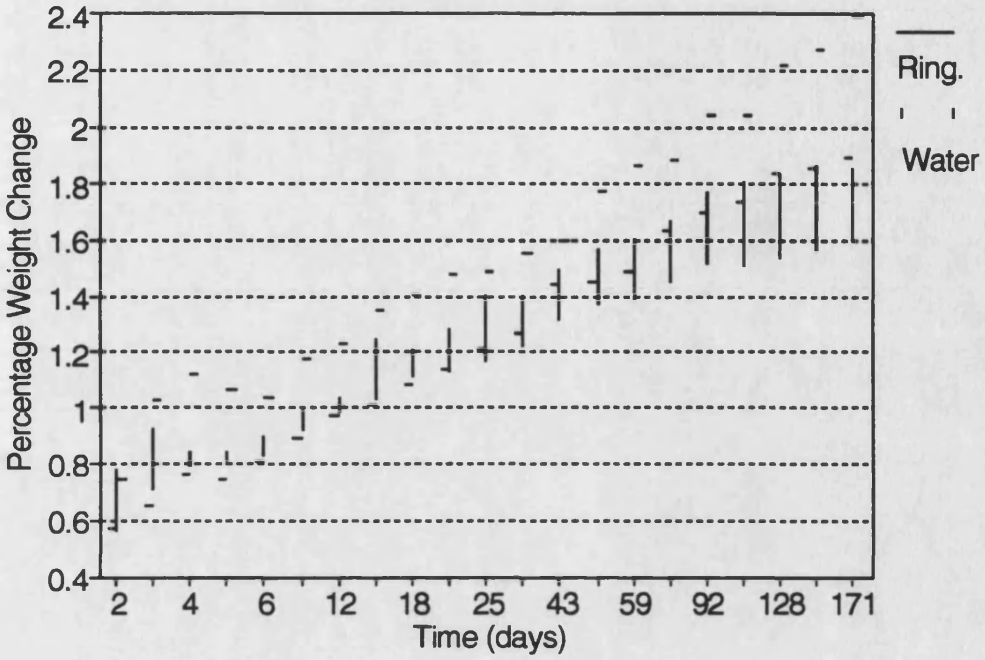


Figure C.38 : 95%CI for Ingress Results for Normal Cement at 37C

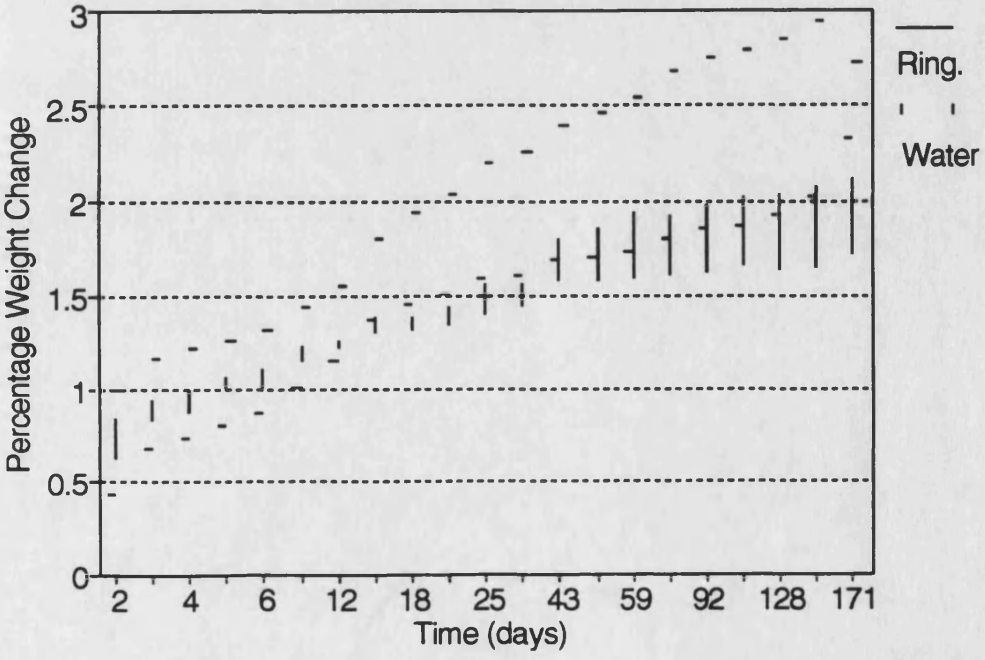


Figure C.39 : 95%CI for Ingress Results for Normal Cement at 21C

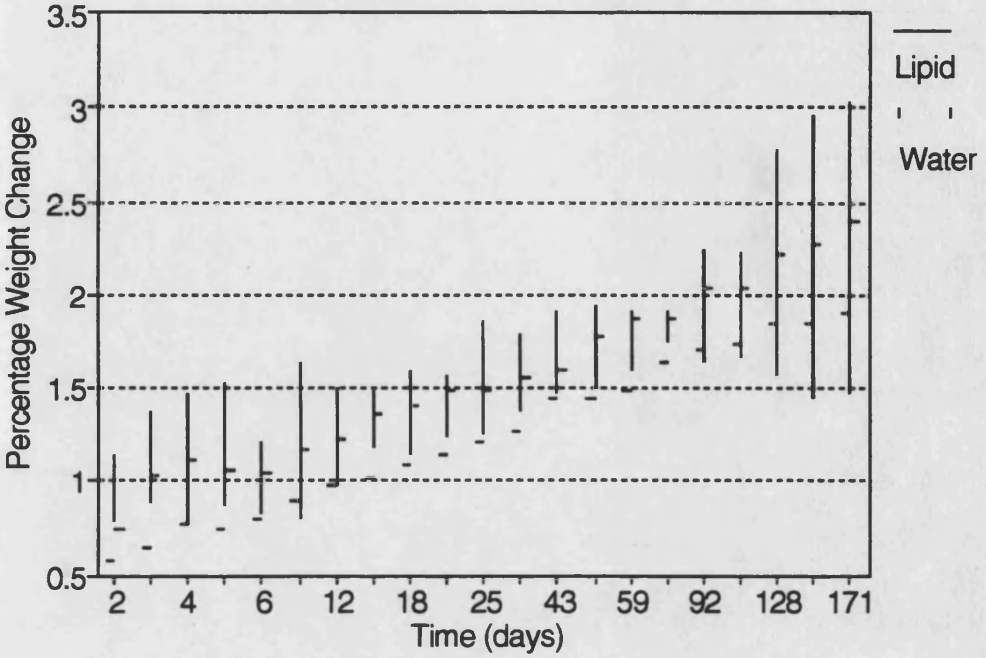


Figure C.40 : 95%CI for Ingress Results for Normal Cement at 37C

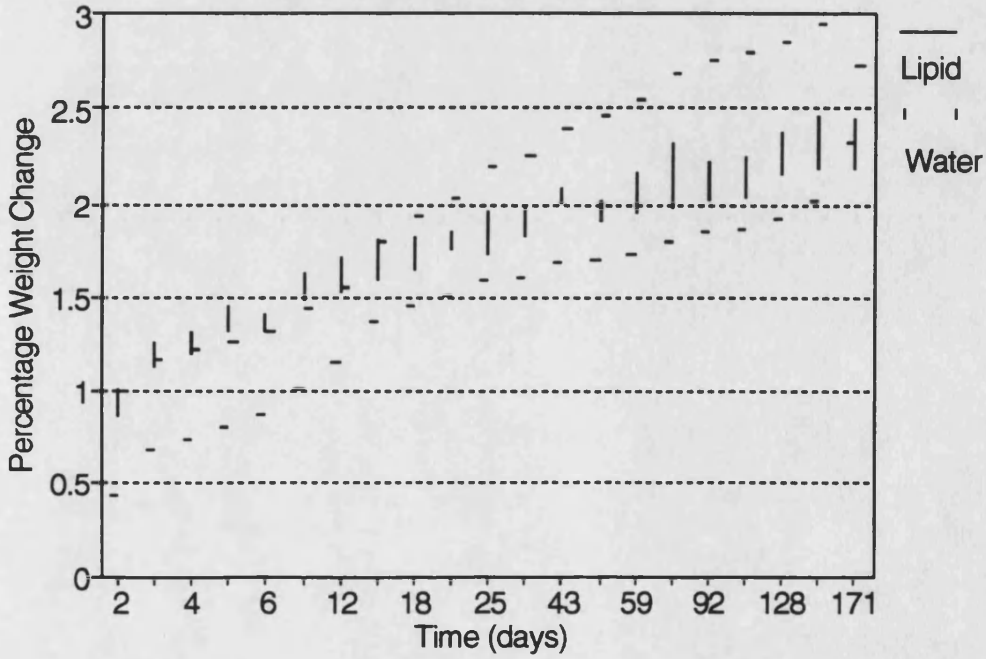


Figure C.41 : 95%CI for Ingress Results
for Fully Cured Cement in Air

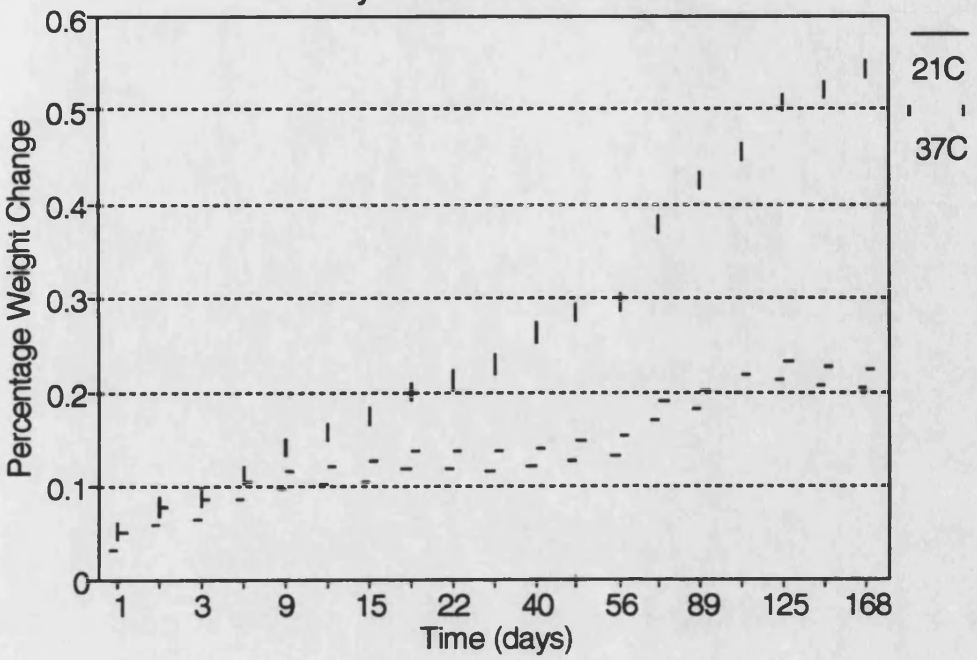


Figure C.42 : 95%CI for Ingress Results
for Fully Cured Cement in Water

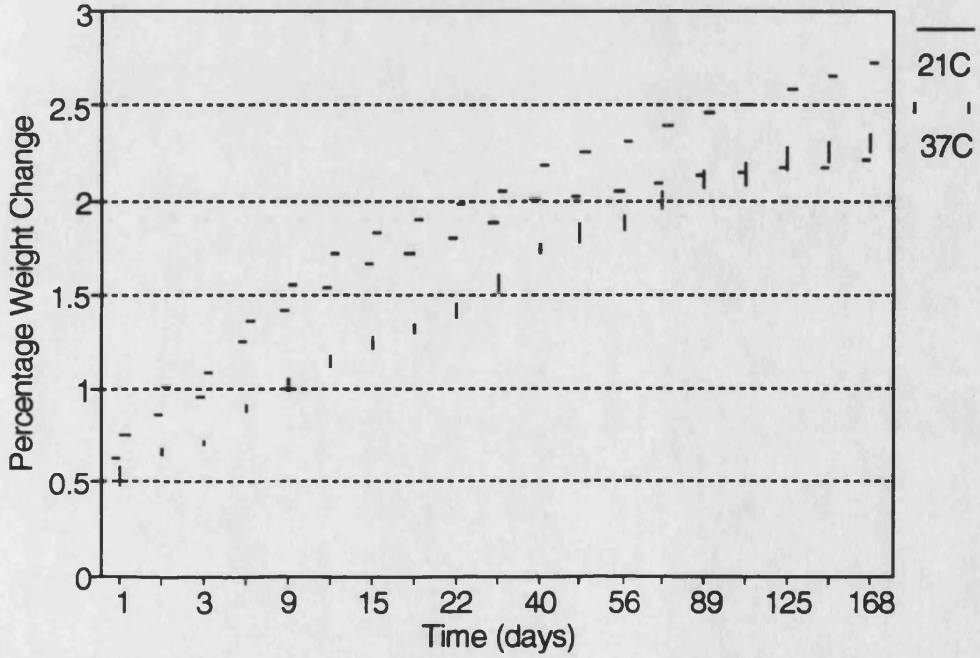


Figure C.43 : 95%CI for Ingress Results
for Fully Cured Cement in Ringer's

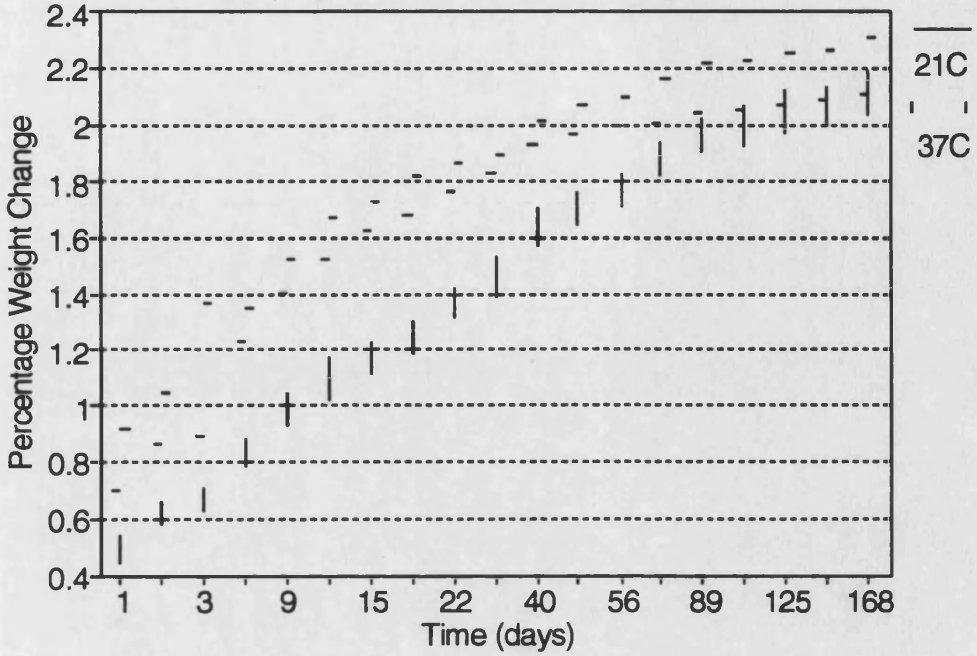


Figure C.44 : 95%CI for Ingress Results
for Fully Cured Cement in Lipid

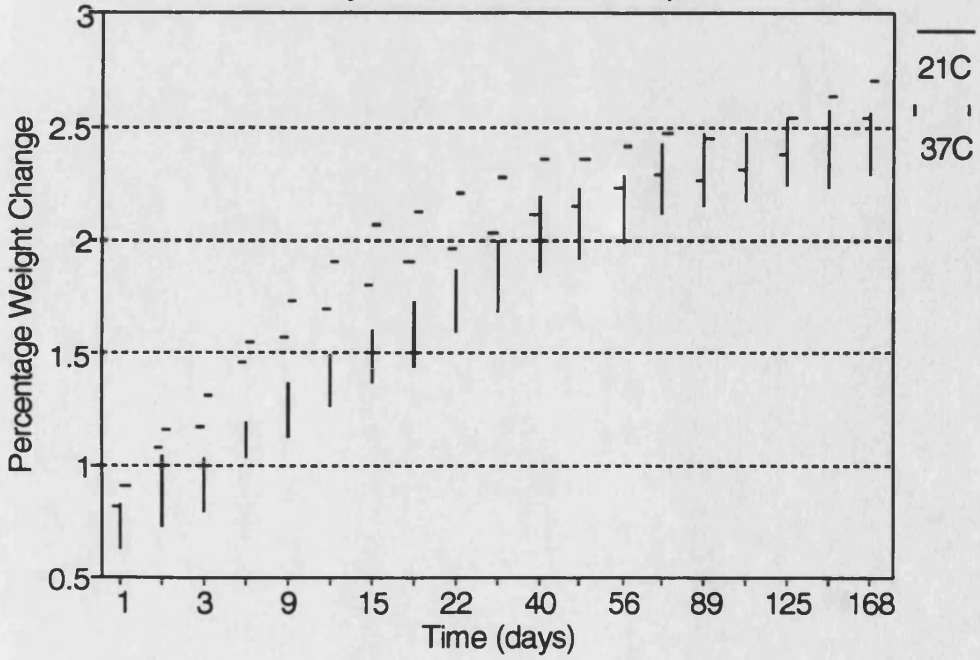


Figure C.45 : 95%CI for Ingress Results
for Fully Cured Cement at 21C

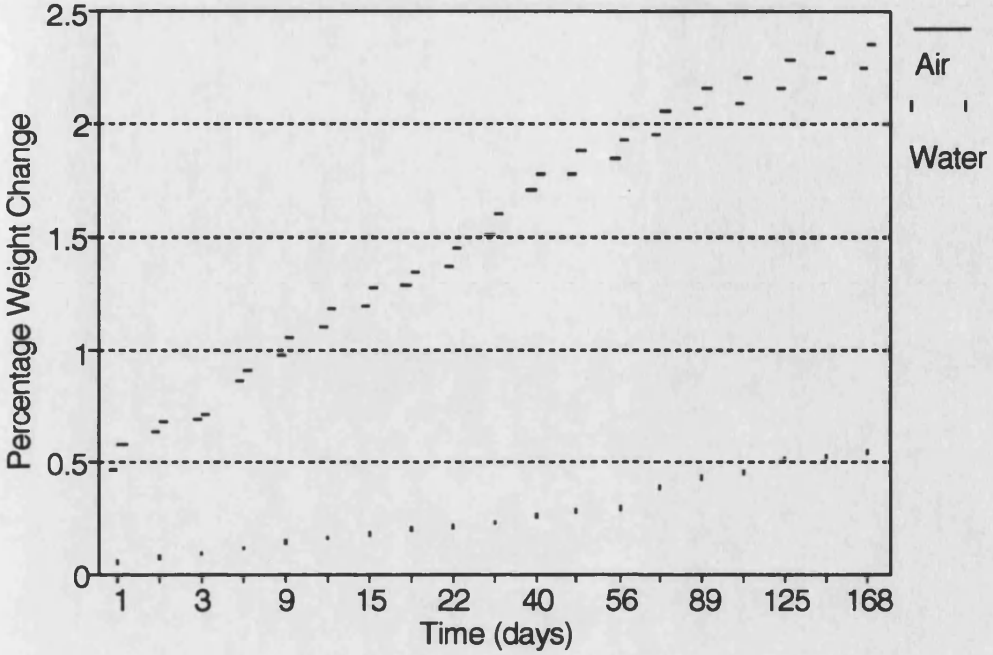


Figure C.46 : 95%CI for Ingress Results
for Fully Cured Cement at 37C

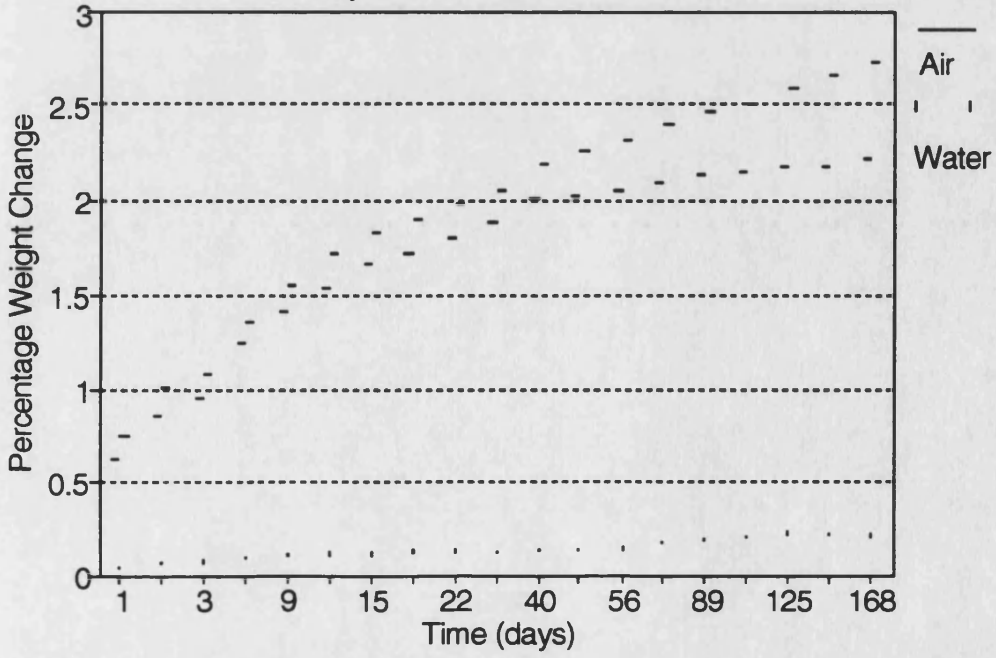


Figure C.47 : 95%CI for Ingress Results
for Fully Cured Cement at 21C

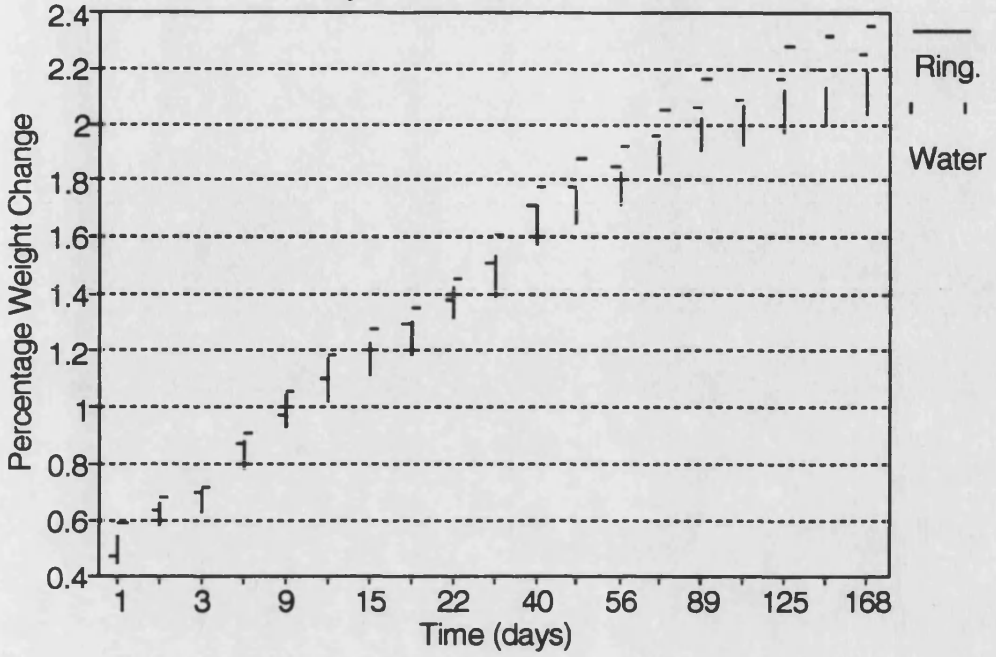


Figure C.48 : 95%CI for Ingress Results
for Fully Cured Cement at 37C

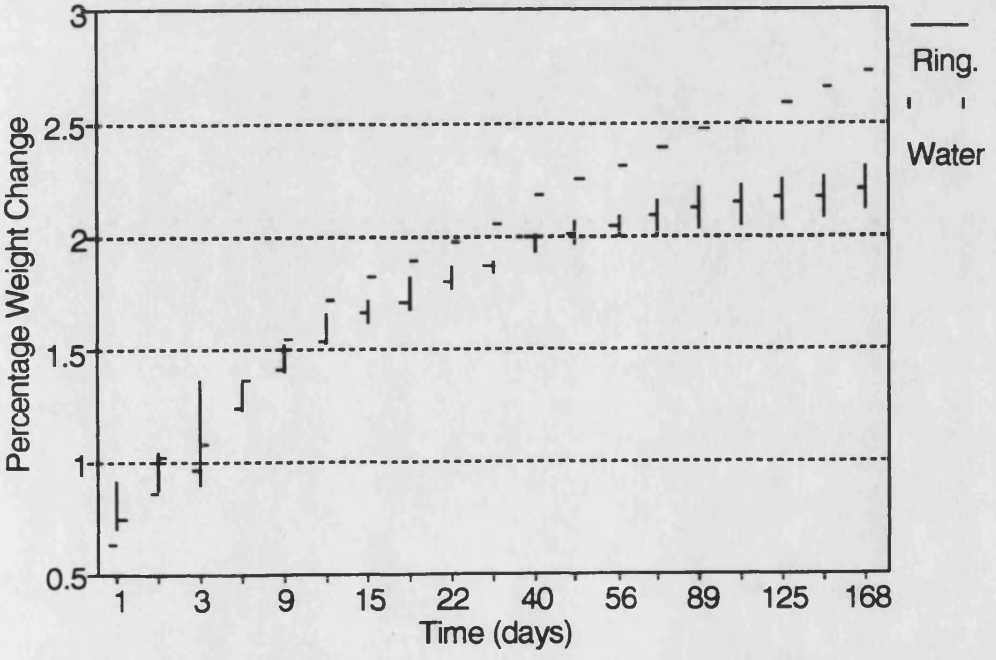


Figure C.49 : 95%CI for Ingress Results
for Fully Cured Cement at 21C

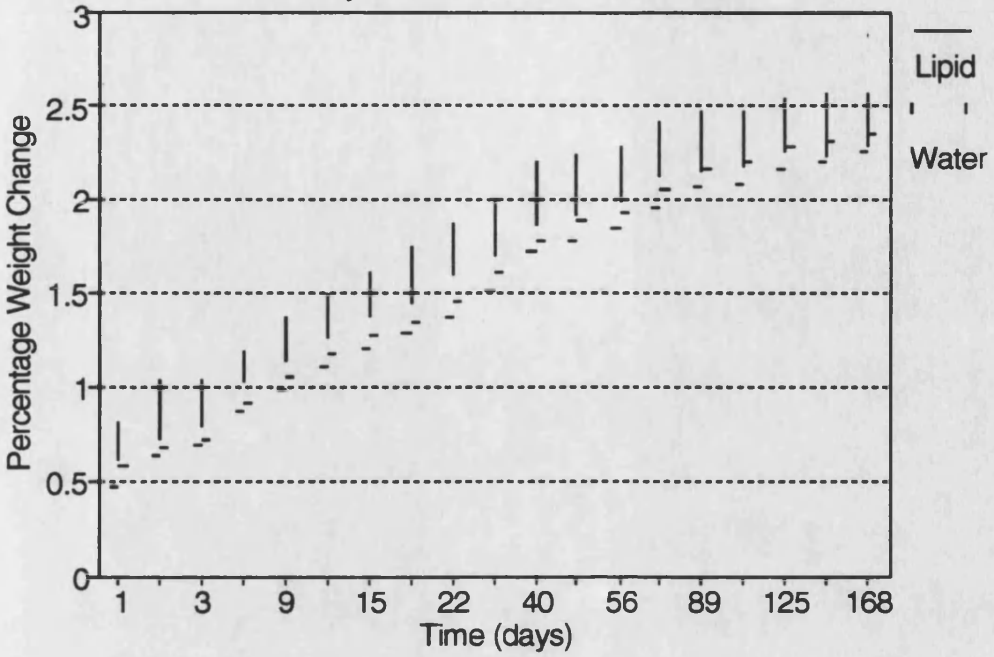


Figure C.50 : 95%CI for Ingress Results
for Fully Cured Cement at 37C

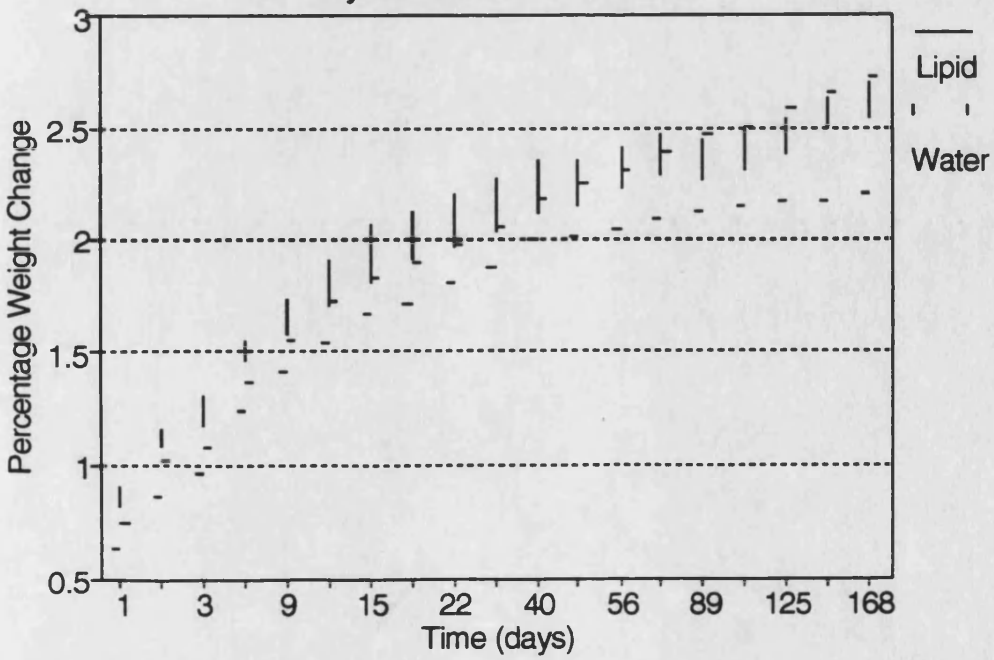


Figure C.51 : 95%CI for GC Results for Normal Cement after 3 Months

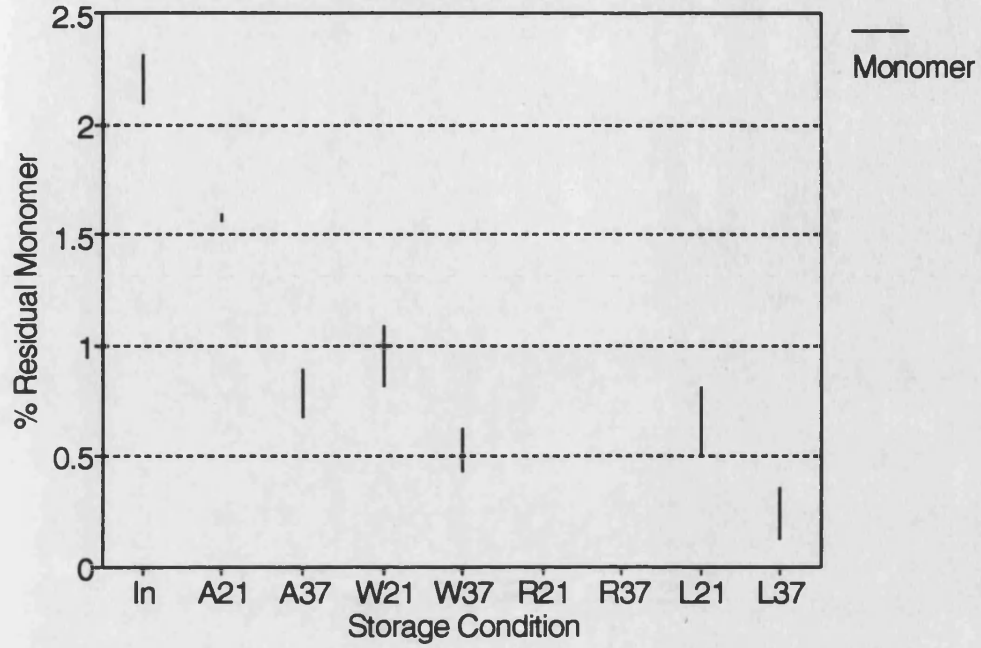


Figure C.52 : 95%CI for GC Results for Normal Cement after 18 Months

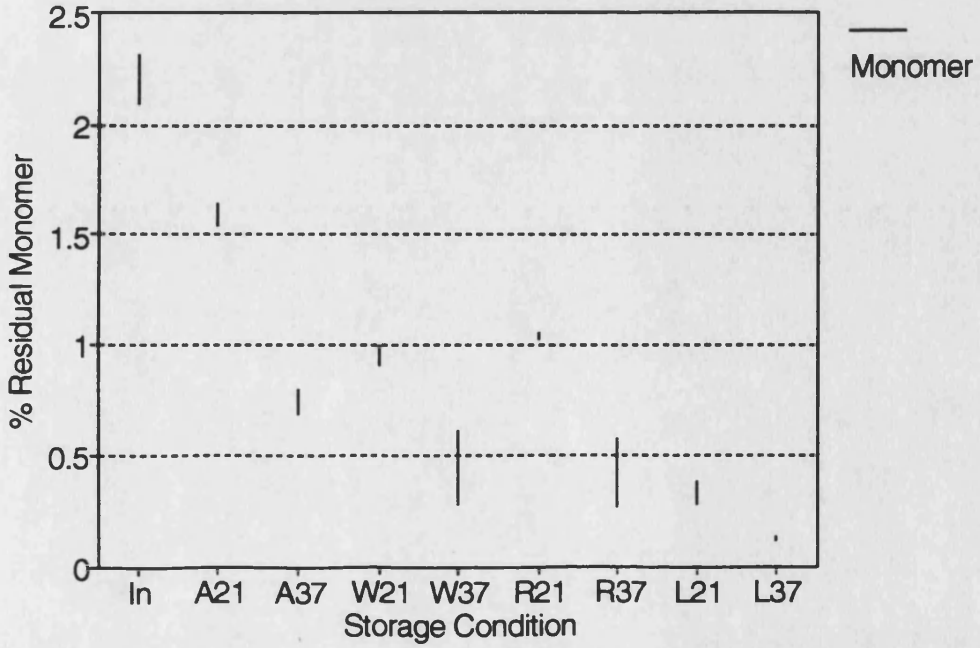


Figure C.53 : 95%CI for GC Results for Fully Cured Cement after 16 Months

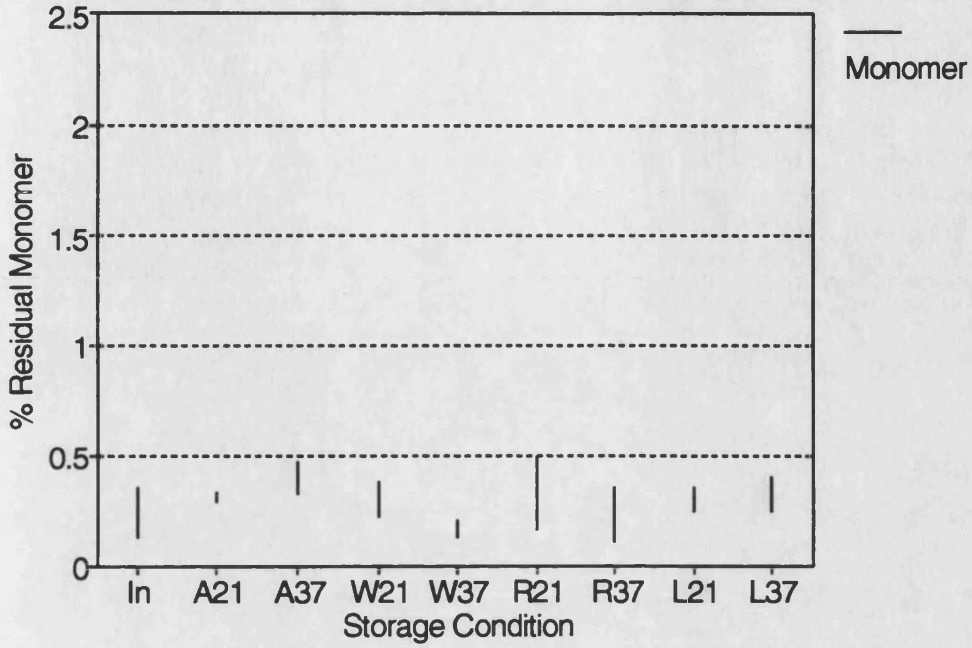


Figure C.54 : 95%CI for Molecular Mass of Normal Cement after 18 Months

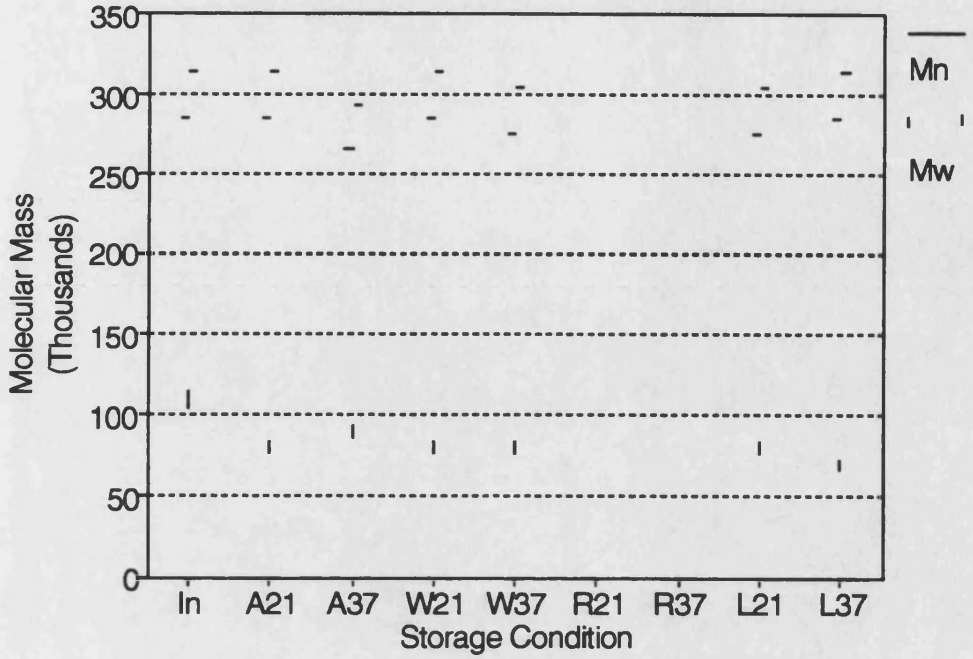


Figure C.55 : 95%CI for Molecular Mass of Fully Cured Cement after 15 Months

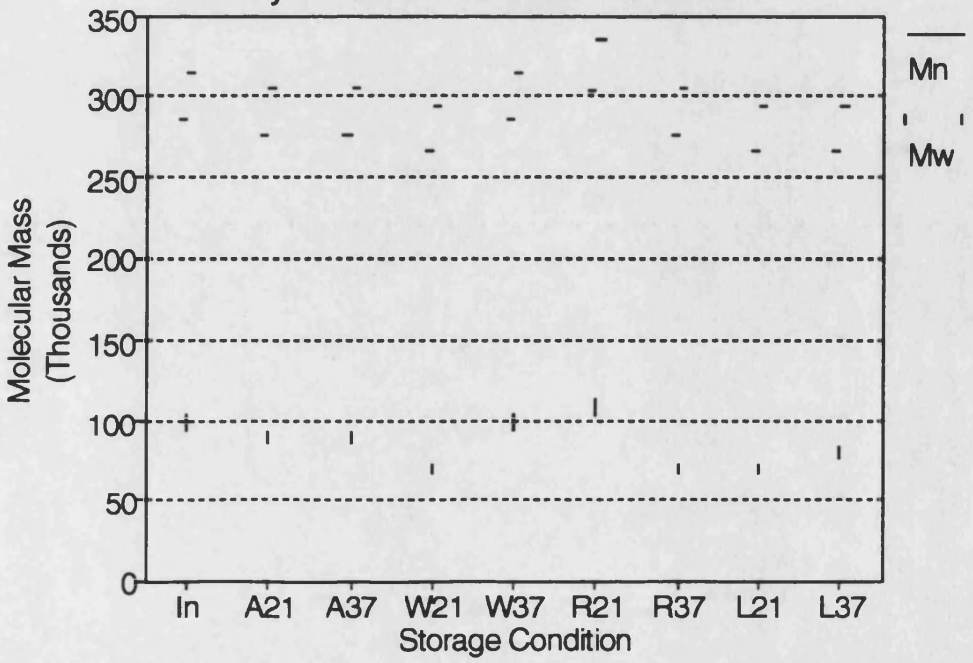


Figure C.56 : Effect of Pre-notching on the WOF for Cement Stored in Water

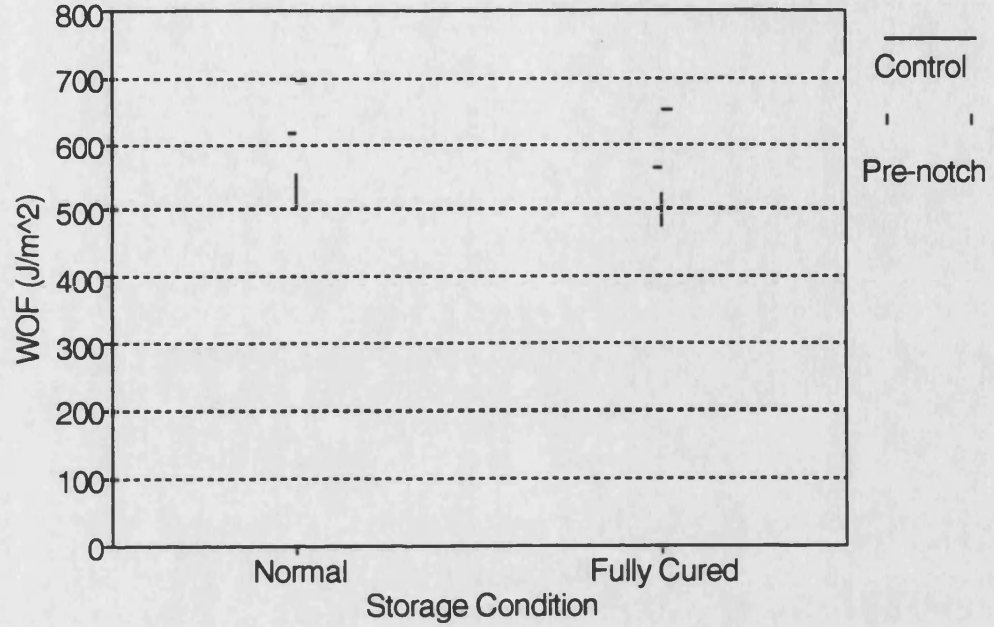


Figure C.57 : Effect of Laboratory Test Temperature on the WOF for Cement